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Assessments through field studies, experiments and modelling of potential risk for phosphorus loss from an agricultural watershed

Dissertation for the degree of Philosophiae Doctor (Ph.D.)

by

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Series of dissertations submitted to the
Faculty of Mathematics and Natural Sciences, University of Oslo
No. 1705

ISSN 1501-7710

Cover: Hanne Baadsgaard Utigard.
Print production: John Grieg AS, Bergen.

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Preface

Everything started with an unexpected conversation on one day in late 2011. “Do you want to study for a doctoral degree? In Norway?” suddenly asked by my unit chief, Dr. Lu. “It is about environmental chemistry and will last 3~4 years.” My instinct said yes right away: ‘of course, I want it’. A doctor degree is my dream and it is a precious opportunity to study abroad. Before I was about to open my mouth, many other things poured into my mind. Can I manage it? How can I communicate with my supervisors and other colleagues with my poor language skills? Will I get along with them with a totally different academic and cultural background? I was practically a layman on environmental chemistry at that time.

“You can think about it over a couple of days, but remember it could be the first and the only chance I can offer you.” Dr. Lu continued.

“I have already made my mind. Yes, I do.” I told him. Challenge accepted!

My Ph.D. study was supported by SinoTropia project, a bilateral cooperation project between China and Norway. This project is an interdisciplinary research projects focusing on freshwater eutrophication in a local watershed in my hometown, Tianjin. A major cause for the impaired water quality is diffuse runoff of nutrients, particularly phosphorus (P), causing eutrophication. The nutrients come mainly from overuse of fertilizer, and unregulated excess dung from husbandry. During my Ph.D. study, I mainly focused on determining the potential risk for P loss from soil to surface water through field studies, experiments and modelling.

This study has enhanced our capability to assess the potential risk for P loss and identify the main factors governing the flux of P from zones with different risk for P loss. These findings may thus be used by policy makers to identify “hot spot” P source regions, and formulate targeted mitigating measures to curb eutrophication. Knowledge and understanding from this thesis have already been used by local authorities while developing a pollution control plan for the reservoir.

Before the end of my Ph.D. study, I hope I have answered all the questions I asked myself in 2011. In the field of scientific research, I'm just a pupil. I am still on the road, and this road will never end.

Acknowledgements

This work has been carried out at the Department of Chemistry, University of Oslo, since March 2012. I would like to express my gratitude to all those who helped me over the last three and half years. There are too many people to thank explicitly in this short acknowledgement, but you know yourself who you are.

My deepest gratitude goes first and foremost to Professor Rolf David Vogt, my supervisor, for his instructive suggestions and constant encouragement through the course of this study. Your office's door is always open for me. I gained strength, courage and confidence after each discussion with you.

I wish to pay high tribute to my co-supervisor, Professor Xueqiang Lu. Dr. Lu is the person who led me into the world of scientific research. His rigorous scientific approach and his personal charm deeply affected my professional attitude. I also would like to thank my second co-supervisor Professor Chongyu Xu. Your selfless assistance, not only with my publications, but also your meticulous care for my daily life is highly appreciated. I will never forget your gracious invitations to each Chinese New Year and loving care after my appendicitis operation, all of which gave me warmth and strength. I would also like to thank Professor Hanlin Zhang and Professor Tore Krogstad for all valuable suggestions and help for my Ph.D. research.

I am grateful to my colleagues in the department of Chemistry (University of Oslo) for their generous assistances. Special thanks to my "Chinese team": Professor Changwei Lv, Dr. Liang Zhu and Mr Xiaoguang Yang. As the perfect instructor and companion for me, Professor Lv gave me great supports during his stay in our group as a visiting scholar. I will never forget all of the fruitful discussions with you. A special thank goes to Dr. Zhu for teaching me the basics in the world of scientific article publishing. The many illuminating suggestions from you have played an instrumental role in improving my publications. I am also indebted to Mr. Yang for your kind assistances during the past three years, not only at work but also in my life.

Special thanks go to my "Norwegian brother" Dr. to be Christian Mohr for many instructive discussions. Thanks to my wonderful office neighbours and fellow Ph.D. candidates, Alexander Engebretsen and Cathrine Gundersen, for your consistent support and refreshing conversations. Thanks also to the former master students of SinoTropia project: Bishnu Prasad Gyawali, Wycliffe Omondi and Ellen Pettersen for your kind assistances during the fieldwork and my stay in Oslo over the past three years. In addition, I would also like to thank all my colleagues at TAES, Dr. Xiaowen

Deng and Ms. Ping Ye for their wonderful analytical job in the lab. Yuqiao Reservoir Administration Department, Ji County Statistics Bureau, and Ji County Land and Resources Bureau are all highly acknowledged for their valuable assistance in providing the essential background data. I would also like to thank the numerous local farmers for their wonderful assistances in collecting samples.

My family also deserve a big thank you for your consistent support making me believe in myself. Words cannot express how grateful I am to my parents for all their sacrifices. Through the past three years, due to the tense research schedule, I have not been able to offer you enough care, even after my father's surgery. Your selfless love will give me strength and courage in my life.

My biggest thank you goes to my wife Ms. Min Si. I really owe you so much over the past 3.5 years. I have not been able to give you a normal married life like other husbands due to living in different continents. There has been nothing more important than your understanding during my study in Norway.

Finally, I wish to acknowledge the Research Council of Norway for their support to the SinoTropia project (Project no. 209687/E40) and my Ph.D. funding. Without their supports, my study in Norway would not have been possible.

Bin Zhou
Oslo, October 2015

List of publications

This dissertation is based on the following articles, which are referred to in the text by their Roman numerals.

I. Zhou, B., Vogt, R. D., Xu, C-Y., Lu, X., Xu, H., Bishnu, J. P. & Zhu, L.: 2014, *Establishment and Validation of an Amended Phosphorus Index: Refined Phosphorus Loss Assessment of an Agriculture Watershed in Northern China*, Water, Air, & Soil Pollution 225, 1-16. DOI: 10.1007/s11270-014-2103-x.

II. Zhou, B., Vogt, R. D., Lu, X., Xu, C-Y., Xu, H., Zhu, L.,Shao, X.,Liu, H. & Xing, M.: 2015,*Relative Importance Analysis of a Refined Multi-parameter Phosphorus Index Employed in a Strongly Agriculturally Influenced Watershed*, Water, Air, & Soil Pollution 226,1-13.DOI: 10.1007/s11270-014-2218-0.

III. Zhou, B., Vogt, R.D., Lu, X., Yang, X., Lü, C., Mohr, C.W, & Zhu, L., 2015. *Land use as an explanatory factor for potential phosphorus loss risk, assessed by P indices and their governing parameters.* Environmental Science: Processes & Impacts 17, 1443-1454. DOI: 10.1039/C5EM00244C.

IV. Zhou, B., Vogt, R. D., Lu, X., C., Mohr, Lü, C. W., Li, X., Deng, X., Shao, X., Liu, Q., 2015. *Effects of land use change on phosphorus levels in surface waters - A case study of a watershed strongly influenced by agriculture*. Submitted to Water, Air, & Soil Pollution.

Other co-authorships:

V. Xie, Z., He, J., Lü, C., Zhang, R., **Zhou, B.,** Mao, H., Song, W., Zhao, W., Hou, D. & Wang, J.: 2014,*Organic carbon fractions and estimation of organic carbon storage in the lake sediments in Inner Mongolia Plateau, China*, Environmental Earth Sciences, 1-10. DOI: 10.1007/s12665-014-3568-z.

VI. Lü, C. W., He, J., Wang, B., **Zhou, B.,** Wang, W., Fan, M., 2015. *Environmental geochemistry of dissolved and biogenic silicon and its nutrient limitation effects in an inland lake, China.* Environmental Science and Pollution Research, 1-11. DOI:10.1007/s11356-015-4322-0.

VII. Xu, H., Xu, C.-Y., Sælthun, N.R., Xu, Y., **Zhou, B.,** Chen, H., 2015. *Entropy theory based multi-criteria resampling of rain gauge networks for hydrological modelling–A case study of humid area in southern China*. Journal of Hydrology 525, 138-151. DOI: 10.1016/j.jhydrol.2015.03.034.

VIII. Xu, H., Xu, C.-Y., Sælthun, N.R., **Zhou, B.,** Xu, Y., 2015. *Evaluation of reanalysis and satellite-based precipitation datasets in driving hydrological models in a humid region of Southern China.* Stochastic Environmental Research and Risk Assessment, 1-18. DOI: 10.1007/s00477-014-1007-z.

IX. Lü, C., He, J., **Zhou, B**., Vogt, R. D., Guan, R., Wang, W., Zuo, L., Yan, D., 2015. *Distribution characteristics of organic phosphorous in sediments from Lake Hulun, China*. Environmental Science: Processes & Impacts. DOI: 10.1039/C5EM00326A.

Abbreviations

AcP	Acid Phosphomonoesterases
AlP	Alkaline Phosphomonoesterase
ANN	Artificial Neural Networks
BPN	Back Propagation Network
CAS	Chinese Academy of Science
CBD	Citrate-Bicarbonate-Dithionite extractable
CEC_e	Effective Cation Exchange Capacity
CHINOR	Research Cooperation with China
DEM	Digital Elevation Model
DPS	Degree of Phosphorus Saturation
DPSIR	Drivers, Pressures, State, Impacts and Responses
EDTA	Ethylene Diamine Tetraacetic Acid
EPB	Environmental Protection Bureau
GC	Grey Combination
GM	Grey Model
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LOI	Loss on ignition
NASA	National Aeronautics and Space Administration
NE-TP	Total NaOH-EDTA extractable P
NMR	Nuclear Magnetic Resonance
OP	Organic Phosphorus
P	Phosphorus
PD	Phosphodiesterases
PP	Particulate phosphorus
PI	Phosphorus Index
PSC	Phosphorus Sorption Capacity
PSD	Particle Size Distribution
PSI	Phosphorus Sorption Index
PY	Pyrophosphatase
RCEES	Research Centre for Eco-Environmental Sciences
RCN	The Research Council of Norway
ROC	Relative Operating Characteristics
SOM	Soil organic matter
STP	Soil Test Phosphorous
TAES	Tianjin academy of Environmental Science
TIP	Total Inorganic Phosphorus
TOP	Total Organic Phosphorus
TP	Total Phosphorus
UiO	University of Oslo
XRD	X-Ray Diffraction

Abstract

China has been facing serious environmental challenges in recent decades. Shortage of treatable freshwater, due mainly to severe water pollution, has become a limiting factor hindering further economic growth and social development in China. Eutrophication, which results in excessive algae growth, has gained huge attentions due to its apparent visible effect and severe damage to the water quality and ecosystem. Numerous studies have identified enhanced phosphorus (P) fluxes from diffuse agricultural sources as one of the most dominant causes for freshwater eutrophication in China. Therefore, identifying the potential risk for P loss is a prerequisite in order to figure out the optimum and most cost-efficient abatement actions against eutrophication.

1st; An amended P index model has been developed in order to achieve an enhanced identification of the potential risk for P loss. It provides a simple and practical method for identifying hot-spot source areas and to estimate their potential for contributing to the flux of P to the surface waters. As a semi-quantitative tool, the validation process is usually a challenge for this type of models due to inadequate data representation relative to large spatial and temporal variation in fluxes. In response, we carried out a comprehensive synoptic soil study and water monitoring. The validation procedure was therefore developed by comparing the modelled average P index values with the corresponding measured P fluxes for 12 different sub-catchments. The results indicate an improved precision in the simulated potential for P loss using the refined P index scheme. The primary finding of this research is that the areas with close proximity to rivers and the reservoir, as well agricultural land around villages, are the main P sources to the reservoir.

2nd; The significance of each input variable included in P index model to the final P index values is still unclear. In a subsequent study, we therefore carried out a relative importance analysis of the 14 input variables. The backpropagation network with Garson's algorithm was employed in order to capture the significance of interactions among the input variables. This study clearly shows that the source factors, especially the degree of P saturation (DPS) along with management practices regarding application of inorganic P fertilizer and livestock manure, are the most important factors governing the P loss in the very high and high risk areas. Conversely, the transportation factors governed P loss risk in the low and very low risk areas. Recommended management strategies for mitigation of P loss from the different risk

zones are proposed based on the relative importance analysis and practical constraints. 3rd; Through previous studies a clear understanding of the spatial distribution of the potential for P loss and the main controlling impact factors for each risk zone were developed. It was found that the relative risk for P loss was closely related to the local land use. It was therefore possible to conduct a study using readily available data on land use as an explanatory factor for assessing potential P loss risk from a watershed. In this study, a set of conventional indicators for soil P loss risk were measured along with the main P pools, P sorption indices, texture, organic matter, as well as Fe and Al oxides and other mineral components. Moreover, detailed soil P speciation was conducted using P nuclear magnetic resonance (^{31}P NMR) spectroscopy. In addition, phosphatase activities in the soils were determined for each land use soil category. The results indicated that most soil samples had relatively homogeneous soil physical priorities. P containing minerals, such as Apatite and Vivianite, were not found in any of the soil samples, which imply that the P in the soil is mainly from agricultural practices. The soil content of total P, total inorganic P and soil test P (STP) (a proxy for bioavailable P) increased significantly following the order of increasing management intensity. STP, being strongly coupled to the application of P fertilizers, was a strong explanatory factor for the spatial differences in DPS – both between and within different land use types. The dominant inorganic and organic P species in the soils were orthophosphate and monoester-P, respectively. Their contents were oppositely correlated with the degree of management influence, with the amount of orthophosphate positively related. Alkaline phosphomonoesterase (AlP) represented the highest activities among the four representative phosphatases, i.e. enzymes that hydrolyze organic P – releasing labile orthophosphate. Orchard soils were found to contain the highest levels of monoester P as well as high AlP activities. This indicates a strong capacity to produce labile orthophosphate. Our studies thus suggest that the readily available data on spatial distribution of land use can be employed as explanatory factors for assessing the potential for loss of P.

These studies were followed up by a study focusing on the effects of land use change on P levels in surface waters. A coupled simulation using Dyna-CLUE model with Grey Relational analysis (GRA) and GM (1, 1) model was employed to simulate the area demand and spatial distribution. In addition a comprehensive land use index, with degree of P saturation (DPS) as weight coefficient, was developed to examine the statistical and spatial relationships between land use and P levels in receiving waters.

An announced emigration and watershed ecological reconstruction plan were designed into the scenarios in order to evaluate its impact of future land use change on water quality. Kappa indexes above 0.85 verified a satisfactory merit for the coupled land use change model. Scenario predictions reveal that the planned abatement actions, comprising local emigration and a comprehensive ecological restoration, will likely significantly decrease the content of P in receiving surface waters.

1. Introduction

1.1 Freshwater eutrophication

Eutrophication is the process of increasing flux of nutrients, such as nitrogen or P. This causes alterations to the aquatic ecosystem (Smith et al. 1999). It usually leads to enhanced growth of aquatic benthic vegetation and phytoplankton and algal blooms, causing a variety of problems such as a spatial depletion of oxygen needed for aquatic fauna to survive. Eutrophication also decreases the value of rivers and lakes as raw water resources for drinking water plants and for recreational purposes due to decreased aesthetics (Chorus and Bartram 1999). In China, agriculture activities have been considered as the dominant contributors to eutrophication through the overuse of fertilizers and unregulated excess dung from husbandry.

1.2 Role of P in the eutrophication issues

P is considered to be the limiting nutrient in most freshwaters (Welch 1978). Increasing the loading of bioavailable P, or bioavailable-ready P compounds, increases thus the primary production (Weiss 1969). Numerous studies have subsequently identified diffusive phosphorus loss from agricultural land as the main cause of water eutrophication in developed countries (Agnew et al. 2006, Elliott et al. 2006). Curbing P loss from terrestrial to aquatic ecosystems has therefore been commonly considered as the most efficient abatement strategies against eutrophication (Correll 1998).

1.3 Water environmental issues in China

China has achieved a remarkable economic growth over the past four decades. Subsequently, it has paid a tremendous toll to the country’s environment. Sustainable economic growth and peoples’ health are increasingly threatened by environmental deterioration and constraints, particularly in the water environment. About 70% of China’s rivers and lakes are significantly contaminated, and 50% of China’s cities have polluted groundwater(Carmody 2010) . This lays serious constraints on the country’s economic and social development (Jin et al. 2005). Eutrophication has been considered as one of the main causes for the deterioration of water quality in China (Smith et al. 1999, Jin et al. 2005). Over the last 30 years the number of eutrophic lakes in China has increased rapidly. The surface areas of waters that are eutrophic add today up to 5000 km^2. An additional 14000 km^2 are in the condition of elevated nutrient load which are now developing into a state of eutrophication (Carmody 2010).

1.4 Models employed in the study

1.4.1 P index model

A simplified P loss indicator (the original P index model) was introduced by Lemunyon and Gilbert (1993) as a proxy to assess the potential for P flux. As a semi-quantitative tool the P index is based on arithmetic computations of source and transportation factors, most of which are readily available data (Bechmann et al. 2005, Buczko and Kuchenbuch 2007). This indicator is therefore an applicable environmental management tool for local water quality managers: In the US the original P index has been routinely applied for assessments of P loss from agricultural fields, and identification of critical areas with high susceptibility for P loss (Stevens et al. 1993, Sharpley 1995a). In Germany, the P index combined with a GIS framework has been applied to identify areas most susceptible for phosphorus leaching (Behrendt et al. 1996). Since the P index was introduced in 1993, the system has grown more comprehensive by incorporating more governing factors: Elliott et al. (2006) introduced the Phosphorus Source Coefficients (PSCs) into the source factor module, enabling the identification of different load rates of dissolved P in runoff from various types of organic fertilizer. Jokela et al. (1998) introduced the role of reactive Aluminium as an important P suppression factor to P index model in acid soils (Jokela et al. 1998, Jokela 1999). In the transport factor module, McFarland et al. (1998) incorporated the distance to water body factor, and Sharpley et al. (2001) introduced the leaching potential factor. More recently, Li et al. (2007) introduced the quality of receiving water factor into the modified phosphorus ranking scheme and Zhou and Gao (2011) adapted the P index in order to use it also in large scale agricultural catchments. Still, the development and implementation of this phosphorus index is in its early stages in China, where a broad application of the phosphorus index system by agricultural managers is yet to be realized (Li and Guo 2010).

The P index model has achieved a great progress through continued additions and perfection. However, as a semi-quantitative tool, P index still contain some shortcomings compared to those based on conceptual physicochemical processes, especially regarding relative poor spatial interpretation capacity and insufficient model validation.

1.4.2 Artificial neural networks and Garson's algorithm for relative importance analysis

Knowledge of relative significance of the individual input variables used in P index model is lacking. Awareness regarding the relative sensitivity of the input factors on the modelling results guides the watershed manager to focus on the most relevant factors thereby improving the explanatory ability of P index. To our best knowledge, only a few studies on this topic have been performed. Brandt and Elliott (2005) conducted a sensitivity analysis of 8 input variables employed in a P index assessment in Pennsylvania, using a partial differentiation algorithm between output and input variables. Similarly, Beaulieu et al. (2006) performed a sensitivity analysis of 10 explanatory variables used in their P index assessment in Quebec by means of the Monte Carlo model and stepwise regression algorithm. Although these sensitivity analysis methodologies are different, both of these studies were based on the assumption that only one input variable varied at a time, while the others were kept constant. The real-world interdependence among P index input variables were thus not taken into consideration in these sensitivity analysis (Mastrorillo et al. 1998, Gevrey et al. 2006). This is problematic as the refined P index clearly demonstrated the importance of these interactions (Zhou et al., 2014). Furthermore, such an approach is not compatible with the concept of the refined P index.

The Artificial neural networks (ANNs) and relevant weight algorithms have provided new thoughts in this field. ANNs are imitations of biological neural networks, akin to the vast network of neurons in human brain. Over the last couples of decades, ANN models have received increased attention and wide application as an intelligent, powerful analytical and forecasting technique in the field of agricultural, environmental and ecological sciences (Lek and Guégan 1999). At present, multi-layer feed-forward neural networks, trained by backpropagation algorithm (BPN), have gained popularity and are applied more often than other networks types . In the BPN all neurons are arranged in successive layers, and the information flows unidirectional from input layer to output layer, through hidden layer(s) with connection weights among adjacent layers (Lek and Guégan 1999, Mumtaz et al. 2008). Garson (1991) proposed an algorithm based on the neural network connection weights in order to determine the relative importance of each input variable, similar to general sensitivity analysis, striving to quantify relationships between explanatory and response variables. However, the main difference lies in the consideration of potential interactions among variables. Using BPN together with Garson's algorithm, all input variables are allowed to vary simultaneously. The magnitude and sign of the relationship between input variables are managed, in compliance with our conceptual understanding. This is thus more equivalent to the real-world condition compared with traditional sensitivity analysis approach using partial derivative algorithm.

The current study assess relative importance of the 14 input variables used in the refined P index and quantifies their individual contributions to the final P index value within each risk classes using BPN with Garson's algorithm. Based on the identified order of relative importance within different risk areas, a series of scenario analysis was subsequently conducted identifying the effect of targeted P loss control strategies in a practical manner.

1.4.3 Dyna-CLUE model for simulation of land use change and its effect on water quality

Anthropogenic activities, especially agricultural actions, have increase the net P storage in terrestrial and freshwater ecosystems by more than 75% compared to pre-industrial levels (Bennett et al. 2001) . Runoff from different types of land use differ in concentrations of pollutants (Tong and Chen 2002). This relationship between land use types and water quality response has been assessed through two main classes of models: In the first class the relationship is modelled by simple empirical relationships based on data from field studies(Quinn and Stroud 2002, Yang and Zhang 2003, Coulter et al. 2004, Godlinski et al. 2004). This commonly renders an insufficient consideration of the effect of land use on water quality at the overall watershed scale; In the another class of models, such as SWAT and AGNPS models (Neitsch et al. 2011), the relationship is interpreted by conceptual physical and chemical mechanisms. However, the application of these models as routine tools for integrated river basin management is severely limited due to heavy data requirements.

Dyna-CLUE model has been broadly applied for spatially simulation of land use change (Verburg et al. 2002). The spatial allocation is based on a combination of empirical analysis of location probability and spatial analysis, and on dynamic simulation of competition and interactions between the spatial and temporal dynamics of land use systems. However, the CLUE model cannot simulate non-spatial land use area requirements. In order to use this model for scenario predictions the future area demand needs be addressed. Grey model system has been widely applied to predict future values of time series based on recent datasets(Wu et al. 2007, Zhao et al. 2007, Cao et al. 2014).Compared with white and black box models, Grey model instead is focused on partially known and partially unknown, which thus provides a technique for determining an appropriate solution for real world problems (Kayacan et al. 2010). It has therefore been applied to predict land use change (non-spatial perdition: area demand).

1.5 Objectives of the study

It is clear that the management of P loss from agricultural land is one of the main means to curb the eutrophication of surface waters in China. A prerequisite for making optimized abatement strategies is to get a clear understanding of the pressures governing the potential risk for P loss and identify the dominating factors controlling mobility and transport of P. The overall object of this work is therefore to gain an improved scientific knowledge of the potential risk for P loss, thereby producing a sound basis for environmental knowledge-based policy making. Specific objectives of this study have been to:

(1) Improve the existing P loss risk assessment system (P index) by modelling a set of small-scale watersheds in which a detailed database was established by compiling existing data and generated high spatial resolution data of soil physiochemical characteristics. In addition P fractions in runoff were monitored in order to enable model validation;

(2) Identify the order of relative importance among 14 input variables within different risk areas in order to get a better understanding of the main pressures and controlling factors affecting P loss;

(3) Identify the effects of different land use on the potential risk for loss of soil P assessed by P indices and their governing parameters;

(4) Increase our understanding of the role of land use on P loadings to receiving waters and to develop an indicator tool for assessing the risk of P loading based on land use change.

1.6 Interdisciplinary and international cooperation

This study has been carried out based on and as an integrate part of the interdisciplinary and Sino-Norwegian bilateral cooperation project SinoTropia (funded by RCN / CHINOR and Chinese Academy of Science (CAS)). This project focused on the watershed eutrophication management in China through system oriented process modelling of pressures, impacts and abatement actions. Using a DPSIR[1] approach on its eutrophication problem we set out to design and conduct coherent and synoptic field monitoring and survey of fluxes of nutrient fractions, thereby laying the basis for an assessment of catchment hydro-biogeochemical processes governing mobilization, transport, and fate of different fractions of P.

The aim of the project was also to improve our understanding of societal processes facilitating (or causing obstacles for) effective abatement policies by conducting an analysis of learning processes and knowledge amongst actors potentially influencing on eutrophication. Through the use of the concept of Circular Economy a nutrient management plan was designed for the Yuqiao reservoir that takes a holistic approach to the challenges of eutrophication, as well as provides relevant authorities and local water users the necessary information for handling health risks and taking precautionary actions.

[1] Drivers, Pressures, State, Impact and Responses

2. Materials and methods

2.1 Site description

The study area is the local watershed of the Yuqiao raw water reservoir for the Tianjin metropolitan and Hebei province (Fig.1) in north-eastern China. The watershed (~436 km^2) has a sub-humid continental monsoonal climate, with an annual mean temperature of 14°C and an average annual precipitation of 653 mm. Nearly three-fifths of the precipitation rains between July and September (JCBS 2011). The area is characterized by a varied topography: Lowlands (with an average gradient of less than 2°) and plains (2-6°) account for 22% and 25% of study area, respectively, thus together constituting nearly half of the watershed. Hilly land with gradients of 6-15°, low mountain region with gradients of 15-25°, and mountain region (> 25°), accounts for 23%, 19% and 11% of the watershed, respectively. On a macro scale the terrain declines from north to south, where the Yuqiao reservoir is situated. The soils are predominantly a mix of Lithosols in the mountains and Gleysols in the lowland. The approximately 130,000 people that reside within the study area have agriculture and husbandry as their main livelihood. Increasing agricultural production is thus one of the main means for increasing income of local farmers (JCEPB 2012).

During the past 10 years, the land use in the watershed of Yuqiao reservoir has been significantly changed or been modified by large-scale conversion of wasteland to agricultural purpose, along with intensified irrigation and cultivation reflecting the rapid growth of agriculture (Li et al. 2012). The lowland and plains are used for growing staple crops, rotating between summer maize and winter wheat, or for vegetable farming. The hilly and mountainous areas are predominantly used for growing either fruits (orchards) or timber (forest).

Eutrophication of Yuqiao reservoir has accelerated over the last decade due to excessive P loading from the land use practices involving application of mineral and organic P fertilizers associated with the intensified agriculture (JCEPB 2012). In an attempt to abate the increasing eutrophication of Yuqiao reservoir the local government, based on advice from environmental research institutions, have formulated and issued massive abatement action plans including deportation of residents around Yuqiao reservoir and an ecological restoration program in the mountain area. According to this plan 28,282 residents around Yuqiao Reservoir will be deported. The restoration program mainly focuses on reducing nutrient flux to the reservoir from the mountain area by converting orchards and timberland to natural forest.

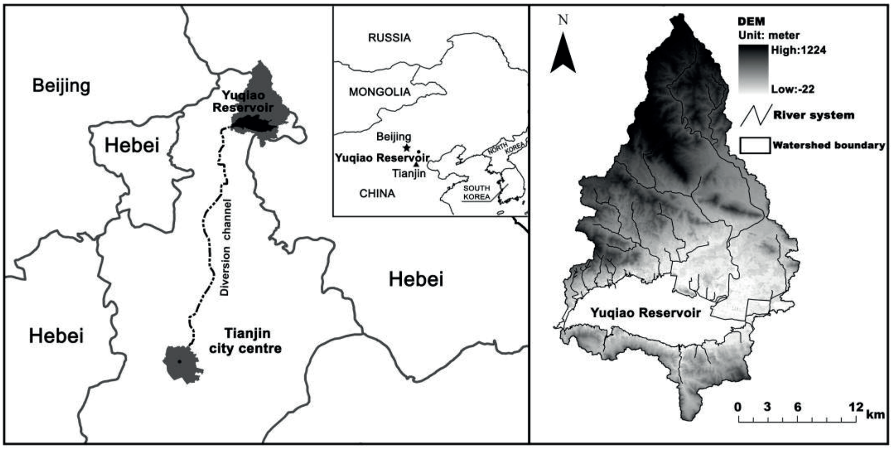

Figure.1 Location of Yuqiao Reservoir local watershed (Paper I).

2.2 Background data collection

2.2.1 Land use data and topographic data

The main land use classification data were provided by Ji County Land Resource Bureau. These data were supplemented by the interpretation of satellite remote sensing data (Quick bird, Landsat TM and ETM).

Topography data (DEM) were downloaded from the United States National Aeronautics and Space Administration (NASA) global digital elevation map webpage[2].

2.2.2 Hydrological and meteorological data

The hydrological data for the Yuqiao Reservoir were supplied by the Yuqiao Reservoir Administration Department. Discharge data for 3 sub-catchments were collected by field monitoring using portable runoff flow-meter during the period from 2012 August to 2013 December by UiO and local staff. Meteorological data were mainly provided by Ji County Meteorological Bureau and the Yuqiao Reservoir Administration Department.

2.2.3 Agricultural management data

Information regarding the general agricultural management was supplied by Ji County

[2] http://asterweb.jpl.nasa.gov/gdem.asp

bureau and Ji County statistics bureau. Some detailed agricultural practice data, such as the method, time and the amount of fertilizer application, were collected through field interviews. The produced amounts of livestock manure as well as domestic sewage and information regarding how this is handled were contributed by the Ji County environmental protection bureau.

2.3 Sampling

2.3.1 Soil sampling

A total of 226 soil samples from 126 different soil sampling sites (Fig.2) were collected in cooperation with Master students from UiO. These sample sites covered the main land use, soil types, agricultural practices and topographical conditions. All samples were composed from 10 sub-samples according to a radial scheme (Wilding 1985). Soil sampling was conducted prior to the seasonal planting and fertilizer application. Sample pre-treatment was conducted according to ISO11464 (2006). Samples for phosphatase assays were stored field moist at 4 ºC, while the rest of the samples were air dried and stored dark at room temperature. The air dried samples were gently crushed by mortar and pestle to break up clods and pass through a 2 mm sieve.

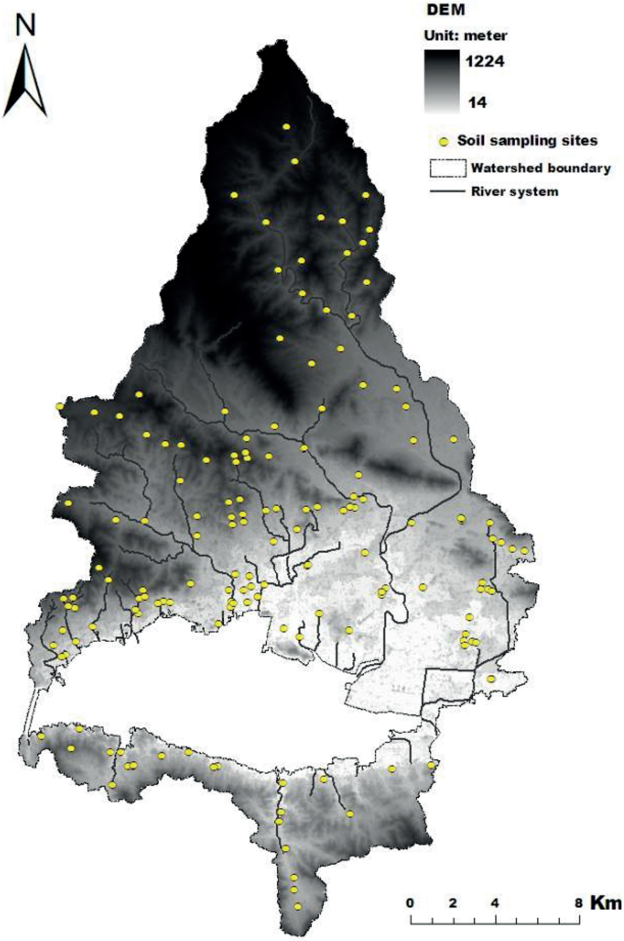

Figure. 2 Location of the soil sampling sites of Yuqiao Reservoir local watershed.

Figure. 3 A cropland soil sampling site.

2.3.2 Water sampling

A total of 287 stream and river water samples were collected throughout the local watershed of Yuqiao reservoir (Fig. 4) during the period from June 2012 to June 2014. The sampling work was conducted in cooperation with UiO Master students and TAES staff. The main flux of P occurs during heavy rainfall periods due to increased erosion and predominance of water flow through upper soil horizons rich in nutrients. More frequent sampling during rainfall episodes were therefore conducted in addition to the routine water sampling. In addition, a total of 30 soil water samples were collected using lysimeter[3] in order to measure the nutrient character of soil solution.

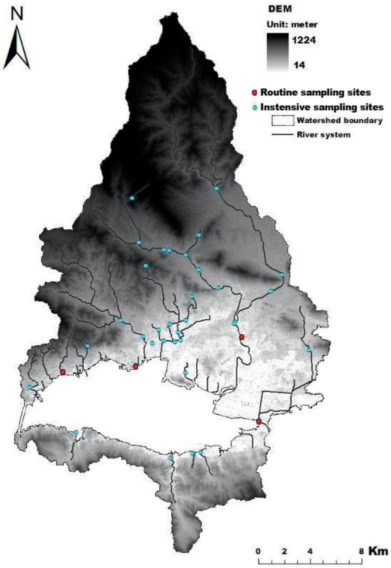

Figure.4 Location of water sampling sites of Yuqiao Reservoir local watershed.

Figure. 5 Water sampling from an outlet of a sub-catchment of Yuqiao Reservoir.

[3] Soil water suction cups

2.4 Soil analysis

2.4.1 General soil properties

Soil pH in deionized water was determined following ISO10390 (2005). Organic matter content was measured gravimetrically according to Krogstad (1992) by determining the loss on ignition. Soil texture of the samples was determined by analysing the particle size distribution (PSD) with a laser diffraction particle size analyser (Beckman Coulter LS 13 320). Sample preparation for the PSD analysis followed the procedure described by ISO11277 (2009). Effective cation exchange capacity (CECe) was determined following the method by Hendershot and Duquette (Hendershot and Duquette 1986), which is comparable to the ISO11260(1994). The exchanged acid- and base cations in the extracts were analysed using Inductively Coupled Plasma Optic Emission Spectroscopy (ICP-OES).

2.4.2 Soil mineralogy

The crystalline mineralogy of the soil was analysed using an X-Ray Diffraction (XRD) analyser (Harris and White 2008) (Bruker D8). The mineral signals were interpreted by software TOPAS 4.2 (BrukerAXS 2008). Amorphous iron- and aluminium oxy-hydroxide were extracted separately with ammonium oxalate (Fe_{ox} and Al_{ox}) (McKeague and Day 1966) and citrate-bicarbonate-dithionite (Fe_{cbd}, Al_{cbd})(Mehra and Jackson 1958), respectively. The contents of Fe and Al in the extracts were analysed using ICP-OES.

2.4.3 P pools and P-sorption indexes

Extraction of organic and inorganic phosphorus pools in the soils was conducted according to the method described by Møberg and Petersen (1982) : Total inorganic P (TIP) was extracted from the soils using hot (70 °C) 6M sulfuric acid. Total P (TP) content was extracted in a similar manner after combustion of the soil sample at 550°C. Total organic P (TOP) was calculated as the difference between TP and TIP. The pool of bioavailable P, referred to as Soil test phosphorous (STP), was extracted using Mehlich-3 reagent (Mehlich 1984). Phosphate concentration in all the extracts was determined spectroscopically using the molybdenum blue method according to ISO6878 (2004) as described by Pierzynski (2000).

P sorption index (PSI), introduced by Bache and Williams (1971), was developed further to rapidly estimate the additional soil P sorption capacity under the existing soil STP content level. It is determined as a single-point isotherm by mixing the soil with an excess of orthophosphate (1.5 mg P g^{-1} soil) (Bache and Williams 1971) and measuring the concentration of non-sorbed P remaining in solution (Sims 2000). The index is given as the ratio of sorbed (*X* in mg P kg^{-1}) over the log concentration of un-sorbed P (*log C* in mg P L^{-1}) according to Equation 1:

$$PSI\ (L\ kg^{-1}) = \frac{X}{\log C} \qquad [1]$$

DPS is a proxy for the degree of soil P saturation and is used to predict risks for P loss (Renneson 2010). Bache and Williams (1971) suggested that the arbitrary numeric sum of STP and PSI could be used as a reasonable relative proxy for soils P sorption capacity (PSC). The sum of soil PSI and STP is therefore applied as a proxy for soil PSC in this study. Degree of P Saturation (DPS) in the soils was thereby determined as the ratio of STP to DPS according to Equation 2 (Wang 2010, Wang et al. 2010).

$$DPS\ (\%) = \left(\frac{STP}{STP + PSI} \right) \times 100 \qquad [2]$$

2.4.4 Soil P species

Phosphorous species in the soils were determined using ^{31}P-NMR. The species were extracted from the soils with a mixture of 0.25M NaOH and 0.11M EDTA (Cade-Menun and Preston 1996, Turner 2008), centrifuged at 10 000g and added a 5% (v/v) mixture of sodium carbonate and sodium dithionite prior to freeze drying (Turner et al. 2003a). The freeze dried materials were transferred to a NMR tube and dissolved in NaOH and D_2O. The spectra were obtained on a 400Hz ^{31}P-NMR spectrometer using 85% H_3PO_4 as an external standard (δ = 0 ppm) via the signal lock (Cade-Menun 2005), and analyzed by MestReNova 8.1 software (Willcott 2009). Peak assignments for the spectra derived from literatures (Turner et al. 2003b, Turner and Richardson 2004, Cade-Menun 2005, Zhang et al. 2013a, Zhang et al. 2013b) were orthophosphate (Ortho-P) at δ =5.7–6.1 ppm, pyrophosphate (Pyro-P) at δ = −4 to −5 ppm, monoesters (monoester-P) at δ = 3 to 6 ppm, phosphonates at δ = 18 to 20 ppm, and terminal and middle polyphosphates (terminal Poly-P and middle Poly-P) at −4 ppm and −19 to −21 ppm, respectively. The total P contents in the extracted NMR samples were determined using ICP-OES. The contents of different species were presented as their relative contribution to this total P.

2.4.5 Phosphatase activities

The activities of four phosphatase enzymes were determined according to the method of Tabatabai (1994). Both acid- (AcP; EC3.1.3.2) and alkaline phosphomonoesterases (AlP; EC3.1.3.1) in field moist soil samples were incubated using p-Nitrophenyl phosphate (PNP) as substrate in their modified universal buffer with pH values of 6.5 and 11, respectively. Phosphodiesterase (PD; EC3.1.4.1) was assayed with bis-p-nitrophenyl phosphate (BPNP) as substrate with a buffer pH of 8. AcP, AlP and PD activities were expressed as the content of p-Nitrophenyl, which was measured spectroscopically at λ=410 nm. Their activities are therefore expressed as mg p-Nitrophenyl kg^{-1} soil (dry weight) h^{-1}. Inorganic pyrophosphatase (PY; EC3.6.1.1) was assayed using sodium pyrophosphate decahydrate as substrate. The assay of PY activity was based on determination of the amount of orthophosphate released when soil is incubated with buffered (pH 8.0) pyrophosphate solution, which was measured spectroscopically at λ=880nm. PY activity was expressed as mg PO_4^{3-}-P kg^{-1} h^{-1}.

2.5 Water analysis

A main focus in the SinoTropia project was on the distribution of P fractions in surface waters. Figure 6 shows the overall scheme of P fractionation. P concentrations in all samples and fractions were determined using the colorimetric molybdenum blue method according to NS-EN-ISO 6878 (2003).

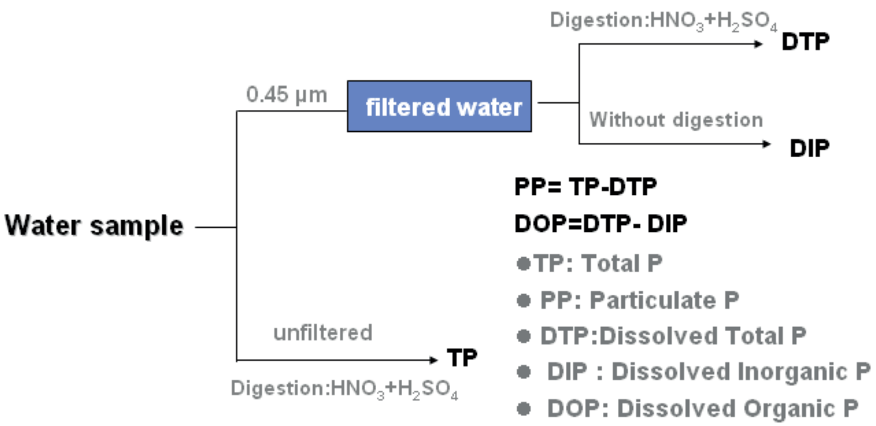

Figure. 6 P fractionation scheme applied on the water samples (Paper I).

2.6 Model development

2.6.1 P index modelling

The organizational structure of the amended P index model is based on the interaction between source and transportation factors (Fig.7). Source factors included an evaluation indicator of soil P saturation (DPS) and three dominating P load factors: fertilizer application, livestock manure and sanitary sewage. Quantization of source factors was based on estimations of their individual contribution to the P load. Transportation factors were organized considering soil properties and general hydrological processes. Detailed descriptions of the methods for calculation of each factor were given in Paper I.

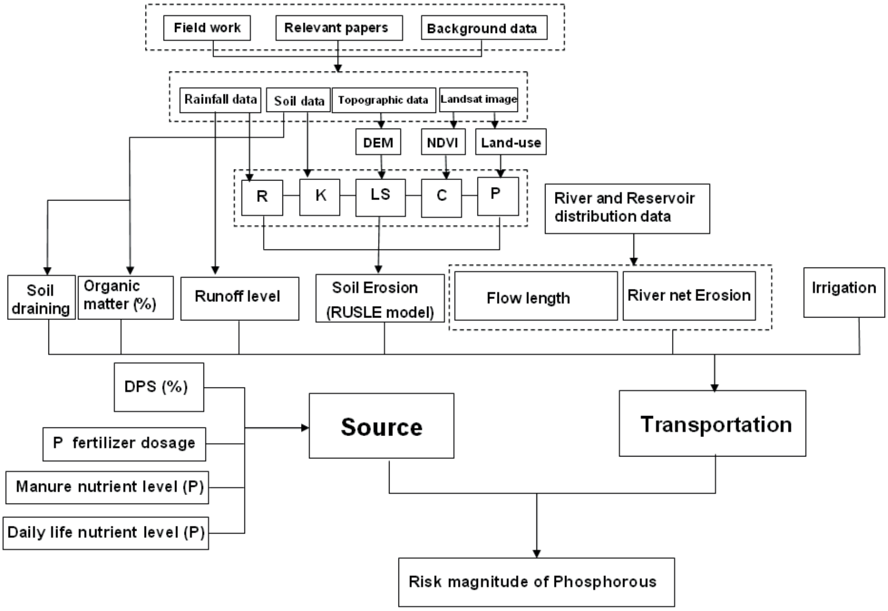

Figure. 7 Structure of amended Phosphorus Index model (Paper I).

2.6.2 Relative importance analysis

2.6.2.1 Multi-layer feed-forward neural network

The algorithm for backpropagation in neural networks consists of the following steps (Lek and Guégan 1999):

(1) Number of nodes (input, hidden and output layer) is set relative to the number of input and output variables,

(2) Learning rates and the maximum iterations (set all weights and thresholds to small random values) are initialized,

(3) Input vectors are given to the input nodes and the output vectors are presented to the output node,

(4) Input values for the hidden nodes are calculated based on Eqn. 3:

$$S_j = \sum_{i=1}^{n} x_i W_{ij} \qquad [3]$$

where x_i is the input variable at the node i, W_{ij} is the weight from input node i to hidden node j.

Then the output was derived from the hidden nodes according to Eqn. 4:

$$Y_j = f(S_j) = \frac{1}{1+e^{-S_j}} \qquad [4]$$

where Y_j is the output variable from hidden node j. The same algorithm was employed to calculate the inputs to the output nodes;

(5) Error term for the output node was calculated,

(6) Iteration ending condition was determined: when the network errors were larger than predefined threshold or the number of iterations was less than the maximum iterations then the calculation process continued (repeat steps 3-5) till one of these criteria was met.

A three-layered feed-forward neural network (one input layer, one hidden layer and one output layer) was employed (Fig. 8). A cross validation method (Olden and Jackson 2000) was applied to determine the optimal number of hidden neurons. It was found that the lowest RMS error was achieved when the number of neurons in the hidden layer was set at four.

The Neural Interpretation Diagram in Fig. 8 shows the structure of the multilayer perception neural network used in this study and its connections between layers.

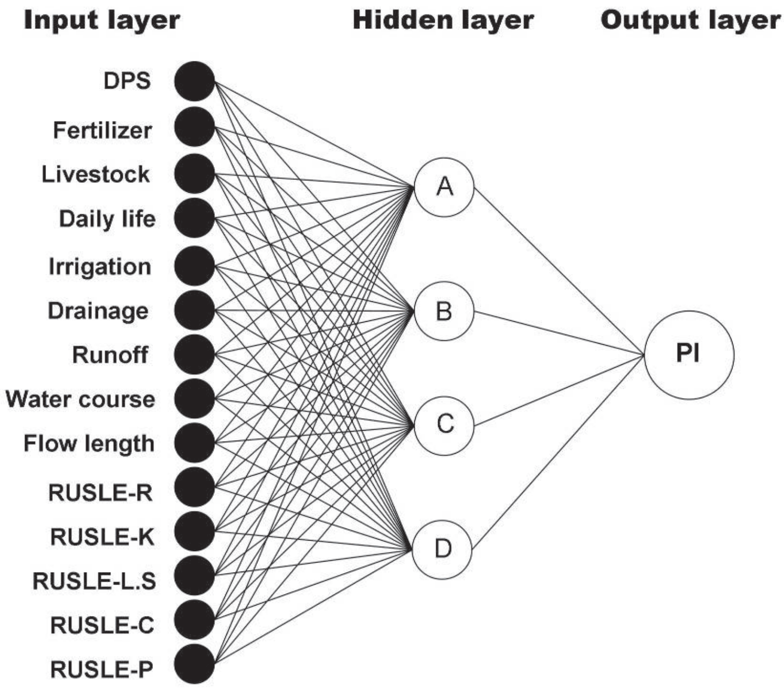

Figure. 8 Neural Interpretation Diagram for interpreting the final PI values as a function of 14 input variables (Paper II).

2.6.2.2 Garson algorithm

Garson (1991) proposed a method of partitioning the neural network connection weights in order to determine the relative importance of each input variable within the network. The same idea has been modified and applied by Goh (1995). The details of the algorithm are given in Eqn. 5:

$$Q_{ik} = \frac{\sum_{j=1}^{L} \left| w_{ij} v_{jk} \right| / \sum_{r=1}^{N} \left| w_{rj} \right|}{\sum_{i=1}^{N} \sum_{j=1}^{L} \left(\left| w_{ij} v_{jk} \right| / \sum_{r=1}^{N} \left| w_{rj} \right| \right)} \qquad [5]$$

where w_{ij} is the connection weight between the input neuron i and the hidden neuron j, v_{jk} is the connection weight between the hidden neuron j and the output neuron k, and $\sum_{r=1}^{N} w_{rj}$ is the sum of the connection weights between the N input neurons and the hidden neuron *j*. Q_{ik} represents the percentage of influence of the input variable on the output. In order to avoid counteracting influence due to positive and negatives values, all connection weights were given their absolute values in the modified Garson algorithm.

2.6.3 Land use change effect on water quality

A flowchart of the methodological structure used in the model to link land use changes to changes in water quality is presented in Fig. 9. It contains three main parts: non-spatial prediction of required area of different types of land use (Part I); spatially allocation of land use (Part II); and prediction of water quality (total P and orthophosphate) based on land use scenarios and land use index (Part III).

2.6.3.1 Land use area requirements (Part I)

This part of the modelling address the issues of "when" and "how much" land use will change for each set of specific scenarios of driving factors. Grey Relational Analysis (GRA) defines situations with no information as black, those with complete information as white and everything between as being grey. In assessments of natural systems one is always somewhere in the grey zone. Grey analysis provides thereby techniques for determining an appropriate solution for these real world problems. Strong cross-correlations between matrix data of macroscopic driving factors and land use area were identified empirically by GRA. Future land use requirements could thereby be simulated by a multiple linear regression model based on the strong relationships between driving factors and their corresponding land use categories. Data from 2004 to 2010 were used to calibrate the model. Validation of the model was conducted by comparing simulated land use to actual land use for the years 2011 and 2012. Predictions of future changes in area of each land use category, based on scenarios of changes in driving factors, were simulated by the developed GRA. The original GM (1.1) was used as a reference land use in order to assess the effect of this novel approach. Both GRA and GM (1.1) models were run using Data Processing System (DPS) software (Tang and Zhang 2013). Further details regarding driving factors and each of the derived models are presented in the Paper IV.

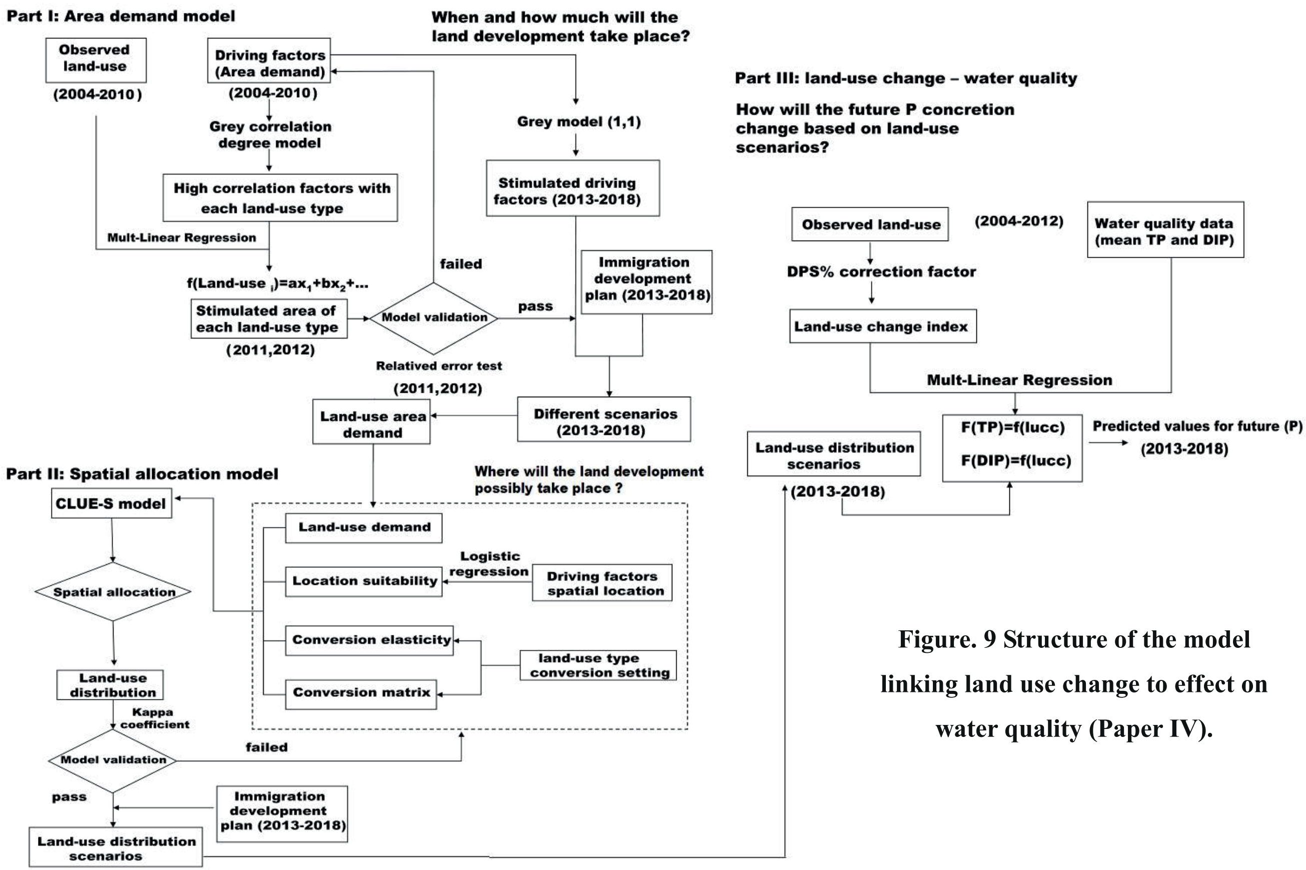

Figure. 9 Structure of the model linking land use change to effect on water quality (Paper IV).

2.6.3.2 Spatial allocation of land use change (Part II)

Land use changes predicted in Part I were spatially allocated using 'Conversion of Land use and its Effects at Small regional extent' (CLUE-S) model (Verburg et al. 2002) based on the simulated area demand data. This addressed the issues of "where" in the overall modelling scheme.

(1) Spatial data

Spatial vector data for land use (year 2004~2012) were provided by the local Land Resource bureau. The data were originally generated from satellite remote sensing images (SPOT 5 and Quickbird) and field surveys of land use. The remote sensing data allowed an allocation of the main land use categories, while field land use surveys provided a more detailed distinction of the land use categories as well as information on related agricultural practices, including irrigation, planting time and fertilizer application. Nine land use types were distinguished: cropland, vegetable field, natural forest, orchard, shrub, timberland, water body, wetland and build-up land. The vector data of land use were converted to grids with high spatial resolution (less than 2.5 m). The spatial data were managed and presented using ArcGIS 9.3 software.

(2) CLUE-S model

The Land use CLUE-S model is developed for spatial simulation of land use changes based on an empirical analysis of location suitability combined with the dynamic simulation of competition and interactions between spatial and temporal dynamics of land use systems.

a. Logistic regression analysis

The probability (P_i) for the occurrence of land use type i in a specific grid cell is given by Eqn. 6:

$$Log(\frac{P_i}{1-P_i}) = \beta_0 + \beta_1 X_{1,i} + \beta_2 X_{2,i} + \cdots\cdots + \beta_n X_{n,i} \qquad [6]$$

where the parameters X refer to the driving factors, n is the number of driving factors, and the coefficients (β_i) are estimated through logistic regression using the actual land use pattern as a dependent variable.

Relative Operating Characteristics (ROC) is a qualitative measure of the regression model fit for each land use category generated by the SPSS 13.0 software (SPSS 2006).

b. Land use conversion matrix and elasticity

Land use policies and land tenure etc. restrict the pattern of land use change (Verburg et al. 2002). In CLUE-S model there are two sets of parameters to reflect the confinement of land use change: land use conversion matrix and elasticity. Restrictions in land use conversions are reflected in a land use conversion matrix which defines to what other land use types the present land use type can be converted (value: 1) or not (value: 0). In addition, each land use type is assigned a factor that represents the relative elasticity to change, ranging from 0 (easy conversion) to 1 (irreversible change).

Land use based on expert knowledge and observed behaviour in the recent past, the conversion elasticities for wetland, water body, shrub, orchard, built-up land, natural forest, timberland, cropland and vegetable are set to 0.2, 0.6, 0.5, 0.6, 0.9, 0.5, 0.6, 0.6 and 0.7, respectively.

c. Allocation procedure

The CLUE-S model allocated land use for each grid cell i by calculating the total probability ($TPROP_{i,u}$) for each land use type u according to Eqn. 7

$$TPROP_{i,u}=P_{i,u}+ELAS_u+ITER_u \qquad [7]$$

where $P_{i,u}$ is the probability for land use type u in location i as calculated in Eqn. 6. $ELAS_u$ is the conversion elasticity for land use u, and $ITER_u$ is an iteration variable that is specific to each land use type u and indicates the relative competitive strength of certain land use types.

d. Validation of land use simulation results

Land use data of year 2004 and 2005 were used to calibrate the model for the parameters and variable settings. Data from year 2006 to 2012 were used to validate the model and to evaluate its simulation accuracy. Kappa index (Eqn. 13) was used to calculate spatial overlap in order to validate the accuracy of the simulation results. The Kappa index evaluates model accuracy by comparing the actual data and the simulation results pixel by pixel (Pontius, 2000). The value of Kappa index ranges from 0 to 1, with unity implying a perfect match (Eqn. 8):

$$Kappa = \frac{P_o - P_c}{P_p - P_c} \qquad [8]$$

where P_o is the observed percentage of agreement, P_c is the expected random correct simulation ratio, Pc=1/n, n is the number of land use types, P_p is the correct ideal simulation ratio, $P_p = 1$.

(3) Scenario analysis

Two different land use change scenarios in the local watershed of the Yuqiao reservoir were assessed in this study: a reference ‘business-as-usual’ scenario based on existing land use development trend without any abatement actions to control the expansion of agricultural land, and a scenario based on the local emigration plan (2013-2018) and ecological restoration program (2013-2018).

2.6.3.3 Water quality associated with land use changes (Part III)

The relationship between P concentration in targeted reservoir and land use change, was assessed in Part III, thereby addressing how future P concentration will change under different land use change scenarios. Different land use types have different risks for P loss. In order to express this distinction a land use weight coefficient based on the degree of phosphorous saturation (DPS) was employed (Eqn. 2). A rather uniform low phosphorus sorption capacity of the soils caused the overall P content and BAP to be mainly explained by land use types and their corresponding agricultural practices. The weight coefficient for each land use category was thus based on their average DPS values. The land use categories Water body and Built-up land were not included in the land use index as they are considered to have no direct P load contribution.

Land use cover change is calculated by Eqn. 9:

$$\text{LUCC index} = \sum_{i=1}^{n} \text{Area}_i \times W_i \qquad [9]$$

where i is each land use type, n is the amount of land use, Area_i is the standardized area of land use type i, W_i is DPS weight coefficient of land use type i.

3. Results and discussion

3.1 Soil P physical-chemical characteristics

3.1.1 Soil properties and P pools

Soil pH values are circumneutral or slightly alkaline, with no significant differences between the land use categories. This pH is consistent with previous studies of soil *pH* in northern China(Hseung 1980) and is due to buffering by carbonate minerals in the predominant sedimentary bedrock. Overall low soil organic matter content (SOM), on the contrary, differs noticeably between land use categories. This is likely due to differences in agricultural management practices among the land use categories. SOM is relatively high in the forest area (6.8%) and lowest in the cropland (3.5%). SOM in the forest soils is mainly derived from the incomplete humification and decomposition of litterfall from the forest canopy. As for cropland, the long-term practice of crop harvesting with removal of the whole plant leads eventually to a depletion of SOM (Wright et al. 2003). A relatively high SOM content was found in the vegetable fields. This is mainly due to the copious application of organic fertilizers (sewage and manure) and plant residues from crop production onto these soils.

The soils had a relatively homogeneous particular size distribution (PSD) with relative low clay content (less than 3%). This texture indicates a relatively easily eroded soil with poor P adsorption capacity(Brady and Weil 1996). Compared to forest and orchard soils, the cropland and vegetable field soils hold a somewhat higher content of fine material (clay and silt). This is most likely the cause for the selected land use by the farmer, rather than an effect. Moreover, cropland and vegetable fields are mainly established on the fluvial flood plains, which are inherently richer in fine material, while orchards and forest are planted on soils developed on steep slopes, from which fine material is efficiently flushed. TIP constitutes consistently the largest P pool and differs substantially between different land use categories. This is clearly attributed to the agricultural practices, pertaining especially to the general practice of applying excessive amounts of inorganic P fertilizer to croplands and vegetable fields. In general, the soils content of TIP increases in the following order: forest < orchard < cropland < vegetable fields. This is consistent with local management data on agricultural practices regarding the applied amounts of P fertilizers. The overall content of TOP was significantly less than TIP in all land use categories. Despite higher SOM content the forest soil had the lowest TOP content (167 mg P kg^{-1}). This is due to the minor or no application of P fertilizers. TOP did not differ significantly between orchards and cropland, though the levels in cropland were slightly lower, despite higher loading of P fertilizers. This is likely due to the lower SOM content, as discussed above, which inherently will contribute to less TOP content in the cropland soils. Vegetable fields showed a relatively high level of TOP (543 mg P kg^{-1}), reflecting both the overall high loading of P fertilizers and the slightly higher SOM.

3.1.2 Effective cation exchange capacity and composition

The soils Effective cation exchange capacity (CECe) and its composition did not differ significant between the four land use categories (Fig.10). Base saturation is high (>85%) with calcium and magnesium being the main exchangeable cations, accounting for 90% of the CEC_E. The acid cations aluminium and manganese thus occupied very small portion of cation exchange capacity (< 7 cmol kg^{-1}). Moreover, exchangeable iron was not detected in any of the soils. This implies that the prevalent carbonate weathering process is rather uniform within the study area and that the influence of agricultural activities on the soil CECe composition is limited. Moreover, the high content of exchangeable divalent base cations indicates that the PO_4 solubility in soil solution is controlled by saturation with calcium and magnesium compounds, such as di- and tricalcium phosphate, through their solubility product.

3.1.3 Soil mineral composition

The crystalline mineral compositions were found to be rather homogeneously distributed in the soils. Quartz (33 ~ 39%), Halloysite (21 ~ 24%) and Muscovite (20 – 27 %) were the main components. In addition, some Albite (4 ~ 7%) was identified in most of the soil samples. Phosphorus containing crystalline minerals, such as Apatite and Vivianite, were not found in any of the soil samples, despite the omnipresence of sedimentary deposits and sedimentary minerals. This was also reported by a local soil nutrient survey (Wang 1982). This implies that the P in the soil is mainly from agricultural practices.

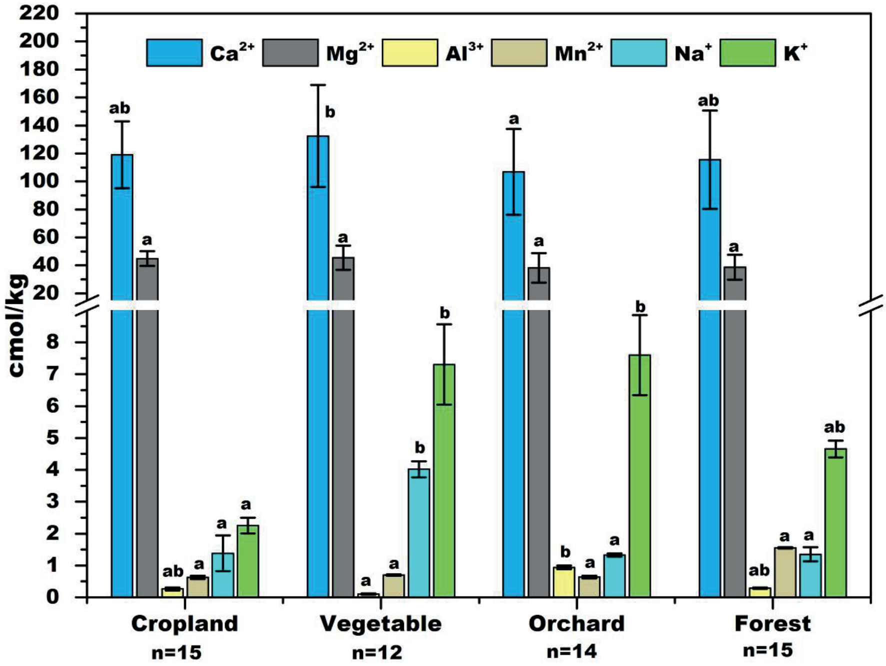

Figure.10 Pools of effective exchangeable cations in soils from four main land use categories (same letter denote no significant difference at 5% significance level (Duncan) and error bars present standard deviations)(Paper III).

3.1.4 Iron and aluminium oxides

The contents of two different pools of Fe- and Al oxides in the top soils are presented in Table 1. Amorphous iron (Fe_{ox}) and aluminium (Al_{ox}) was present in similar amount within each land use category. Their average contents were slightly higher in cropland and vegetable fields relative to forest and orchard. This is likely mainly related to differences in soil-forming factors, especially time and weathering condition (Stewart 1988) between the lowlands and mountainous regions. Some studies have found that the content of amorphous Fe and Al oxides may also be influenced by long-term agricultural practices by changing the SOM level, which might have an inhibiting effect on the crystallization (Schwertmann 1964, Nayak et al. 1999). This may be part of the reason for the slightly higher amorphous levels in the vegetable fields.

Amorphous Fe and Al oxide (Cornell and Schwertmann 1996) forms have greater P sorption capacity than their well-crystalline forms due to their higher specific surface area (Torrent et al. 1990, Nilsson et al. 1992). Considering the generally low organic matter content (Chapter 3.1.1) these relatively large amounts of Fe_{ox} and Al_{ox} are likely the main governing factors for the differences in P sorption capacity between the land use categories. The CBD extractable iron (Fe_{cbd}) values are generally higher than Fe_{ox} oxides, implying a dominance of crystalline Fe over amorphous forms. This is also found elsewhere by other studies (Kparmwang 1993, Raji et al. 2000). Al_{cbd} was not present at higher level than Al_{ox}, with ratios between Al_{ox} and Al_{cbd} ranging from 0.96 to 1.7. These high ratios reflect that Al is mainly present in amorphous forms (Parfitt and Childs 1988, Börling et al. 2001).

Table 1
Levels of amorphous (ox) and crystalline (cbd) iron and aluminium in the soil top A horizon.

Land use	Horizon	Al_{ox}	Fe_{ox}	Al_{cbd}	Fe_{cbd}
		(mmol kg^{-1} soil)			
Forest (n=14)	A	$52±8_a$	$50±10_a$	$54±8_b$	$208±22_b$
Orchard (n=14)	A	$48±6_a$	$48±12_a$	$41±5_{ab}$	$215±25_b$
Cropland (n=14)	Ap	$55±6_b$	$56±5_b$	$36±3_a$	$183±10_a$
Vegetable fields (n=14)	Ap	$58±6_b$	$58±8_b$	$34±3_a$	$182±18_a$

Values are the mean ± standard deviation, and values within a row for each property with the same letter are not significant at 5% level (Duncan) (Paper III).

3.1.5 P sorption indices

STP measured in cropland and vegetable field soils were significantly higher than in the orchard and forest soils (Fig. 11a): The mean value of STP content in forest soil was less than 20 mg kg^{-1}, while it ranged from 90 mg kg^{-1} to 410 mg kg^{-1} in the soil from the vegetable fields. This was as expected considering that background values of natural P are low and that the STP levels in the cropland and vegetable fields are significantly affected by the long term application of excess P fertilizer.

Low PSI values (Fig. 11b) imply that the soils have very poor P sorption capacities. The cause for this is partly owing to few adsorption sites, due to the low *SOM* content, poor soil texture with predominance of 1:1 type clays, and partly due to the heavy loading of P causing a high PO_4 saturation in the soil. The PSI values of forest soils were higher than in the other land use types. This could partly be due to that only a limited number of the available P sorption sites were occupied, and partly due to the higher SOM content, increasing the sorption capacity of the soil through trivalent cation bridging mechanism: Phosphate binds to SOM through ternary complexes, with cations like Fe (III) and Al (III) serving as bridging metal centres between phosphate anions and the negatively charged organic functional groups (Bloom 1981, Haynes and Swift 1989, Gerke and Hermann 1992, Gerke 1993a, b). The soils in orchard, cropland and vegetable fields possessed rather similar, though slightly higher PSI values in vegetable fields.

PSC values (Fig. 11c) in cropland and vegetable fields were higher than in forest and orchard. This may mainly be due to their relatively higher content of amorphous Al and Fe oxides (Table 1), increasing the P sorption capacity (Torrent et al. 1990, Nilsson et al. 1992). It may also partly be owing to slightly higher clay contents, which is commonly related to higher specific surface area, although 1:1 type clays predominate.

The mean DPS values for cropland and vegetable field soils in the study area were 55% and 57%, respectively, while the forest soils had DPS values that were consistently (except one outlier) below the threshold limit of 25% (Fig. 11d), which has been suggested in previous studies(Breeuwsma et al. 1995, Schoumans and Groenendijk 2000) as a critical threshold value, above which the potential for P loss become unacceptable.

This implies that there is an unacceptable high potential for P loss from all the studied land use categories with exception of forests. In general, differences in DPS among the land uses are consistent with the local amount of applied fertilizers. It is noteworthy that the croplands and vegetable fields, consisting of soils with high potential for P loss, are mainly located in the plain area adjacent to the surface water reservoir suffering eutrophication (Zhou et al. 2014).

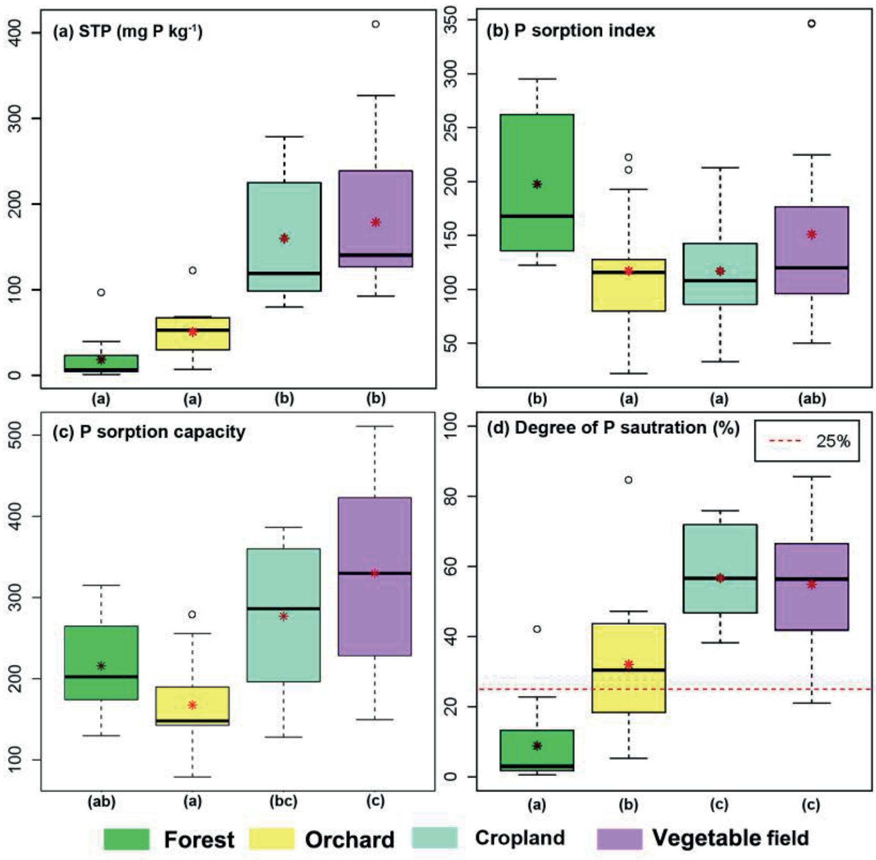

Figure 11. Box plot of potential phosphorus loss indices: a) Soil Test P (STP), b) P sorption index (PSI), c) P sorption capacity (PSC) and d) degree of P saturation (DPS). Red stars denote mean value. Land use with the same letter within each parameter are not significant different at 5% level (Duncan). Open circles denote outliers (Paper III).

3.1.6 Phosphorus species

Concentration and distribution of P species in each of the four main land use categories are given in Table 2, and four representative ^{31}P NMR spectra for each land use type are shown in Figure 12.

Orthophosphate is the predominant P specie, accounting for 62-93% of the total P extracted (NE-TP) from the soils. This is consistent with findings in other studies (Turner et al. 2003c, Reitzel et al. 2006). There is a clear gradient in absolute and relative content of orthophosphate between the four main land use categories (forest, orchard, cropland and vegetable fields). Generally the orthophosphate contents and its ratios to NE-TP increased with increasing agricultural management intensity: The mean orthophosphate level in forest soil was only 79 mg P kg^{-1}, while the values for cropland and vegetable field soils were 360 and 770 mg P kg^{-1}, respectively.

There were no clear differences in the overall low (around 3 mg P kg^{-1}) pyrophosphate content among the orchard, cropland and vegetable field soils. By contrast, the average pyrophosphate content of forest soils was relatively high, i.e. 7 mg P kg^{-1}, accounting for 4.5% of NE-TP. This is most likely due to differences in the soils content of soil microorganism, as pyrophosphate in soils is generally considered to be the product of their metabolism (Ghonsikar and Miller 1973). In general, undisturbed soils commonly contains more soil microorganisms since the quantities, as well as species diversity, of microorganism are reduced by agricultural management (Kara and Bolat 2008).

The average content of polyphosphate was less than 2.3 mg P kg^{-1}. This low level of polyphosphate in the soils may be due to its poor stability (half-life = 0.8 year)(Zhang et al. 2013a). On the other hand, under alkaline conditions, polyphosphate may be completely hydrolysed into pyrophosphate and even partially to orthophosphate (Ahlgren et al. 2005, Reitzel et al. 2006). The addition of NaOH–EDTA, used as an extraction solution, may thus have resulted in de-polymerization of the polyphosphate actually present in the soils extracts.

Orthophosphate monoester-P was the major soil organic P (OP) specie in the soils, accounting for between 6 and 29% of NE-TP. The soils content of monoester-P was found to decrease with increasing intensity of the agricultural management (i.e. forest > orchard > cropland > vegetable fields). This negative relationship is also found in other studies (Condron et al. 1990, McDowell and Stewart 2006) and is explained by increased soil disturbance with increasing management intensity.

Generally, inositol phosphates are considered to be rather immobile and thus non-bioavailable due to their strong binding to clay, organic matter and metal oxides in the soils (Turner et al. 2005, Leytem et al. 2007). On the other hand, inositol phosphates are gaining increased attention due to their potential bioavailability once in solution and subsequent contribution to eutrophication (Turner et al. 2002). The general content of inositol phosphates was found to be relatively low, with average values ranging from 0.9 to 5.8 mg P kg^{-1} (Table 2). This is especially the case for the

Scyllo-inositol phosphates, which was only detected in few samples. The low content of inositol phosphates may be related to the relatively low vegetation abundance, as well as low clay and organic matter content (Turner et al. 2002) of the soil. Therefore, it indicated the relatively active monoester phosphates, such as glycerol phosphate, single nucleotide phosphate, glucose phosphate, were likely to constitute the majority of monoester phosphate group.

The orthophosphate diester group, being the backbone of DNA and central in phospholipids, showed also relatively low content in the soils. Turner and Engelbrecht (2011) reported that DNA is liable to accumulate in cold, wet and acidic soils, while relatively high soil pH condition enhance degradation of DNA. It is worth mentioning that RNA was not detected in practically any of the soils. This is most likely an artefact due to the rapid hydrolysis of RNA under the alkaline conditions generated by the NaOH-EDTA extraction (Turner et al. 2003b).

Similar to the orthophosphate diester, the phosphonates were also only found at relatively low concentrations. This could again be due to their poor stability in alkaline solution as well as their inefficient extraction (Zhang et al. 2013a).

The consistent trend of absolute and relative increase in orthophosphate and decrease in monoester-P with increasing intensity of the agricultural management, among the four land use categories, substantiate land use as a key explanatory factor for the spatial variation in soil phosphate chemistry.

However, only a well understanding of P fractions is still inadequate from the perspective of environmental research. Because not all P species can be directly taken by plants or algae, and phosphatases play the key role of the mineralization process of P through hydrolysis of ester–phosphate bonds(Nannipieri et al. 2011). Hence, a discussion about soil phosphatase activities has been addressed as following chapter.

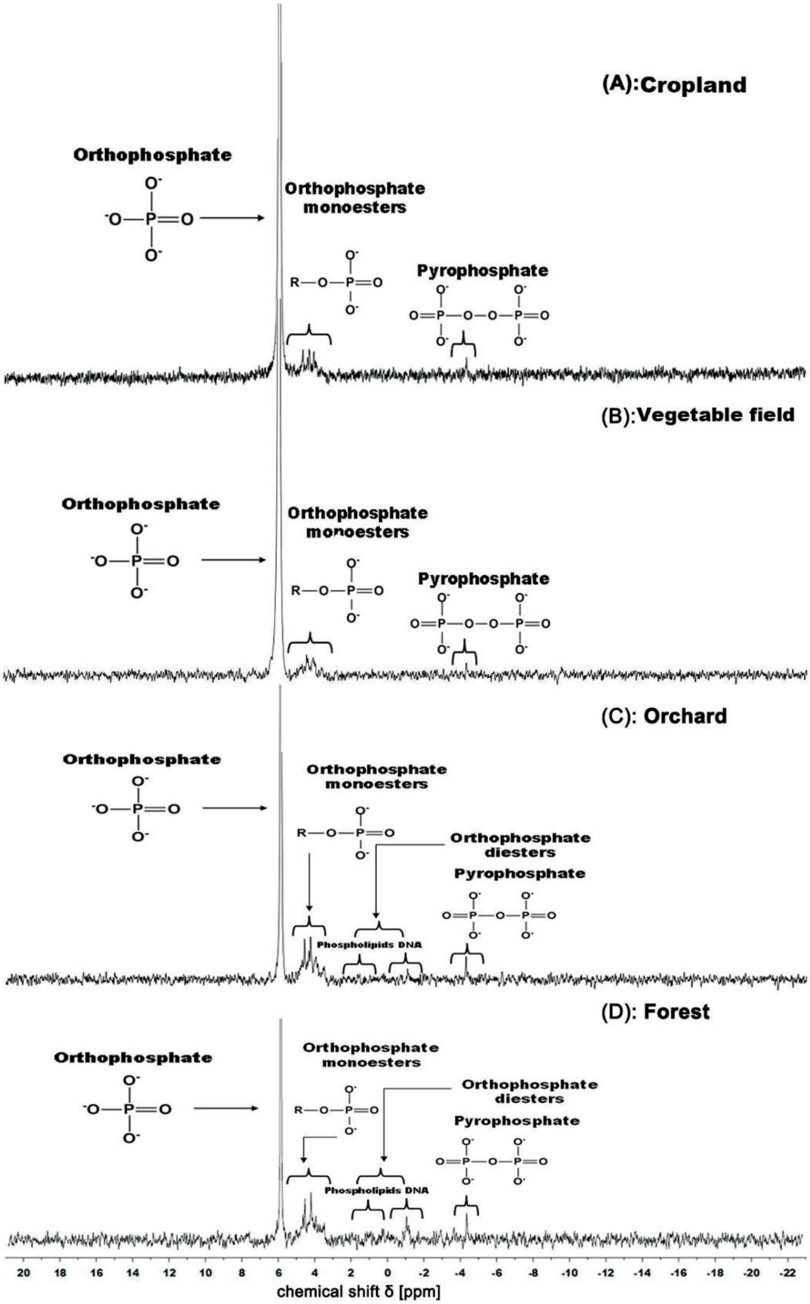

Figure.12 Selected ^{31}P NMR spectra of NaOH-EDTA extracts of the four main land use types (Paper III).

Table 2
Levels (mg P kg^{-1} soil) of different P species within different land use types and their proportions to total P in NaOH and EDTA extracts.

Land use	NE-TP	NMR-P_i			NMR-P_o					
					Monoester-P			Diester-P		
		Ortho-P	Pyro-P	Poly-P	Total monoester-P	Inositol -P		PL	DNA-P	Phos-P
						Myo-	Scyllo-			
Forest	155±12$_a$	79±7$_a$ (50.7%)	7±0.6$_b$ (4.5%)	2.3±0.2$_{ab}$ (1.5%)	63±5$_a$ (40.9%)	4.4±0.4 $_b$ (2.8%)	2.4^{ii} (0.8%)	1.3±0.5^{iii} (0.8%)	0.7±0.01 (0.5%)	2.1±0.2 (1.4%)
Orchard	374±15$_b$	287±14$_b$ (76.7%)	3±0.5$_a$ (0.8%)	1.5±0.1$_a$ (0.4%)	80±6$_c$ (21.5%)	3.1±0.2$_{ab}$ (0.8%)	3.0^{ii} (0.8%)	1.6±0.4 (0.4%)	0.1±0.02 (0.03%)	1.1^{ii} (0.3%)
Cropland	409±127$_c$	360±13$_b$ (88.1%)	2.9±0.1$_a$ (0.7%)	2.3±0.3$_{ab}$ (0.6%)	39±6$_{bc}$ (9.7%)	5.8±0.3$_c$ (1.4%)	2.8^{i} (1.2%)	2.5±0.3 (0.9%)	0.4±0.03^{iii} (0.2%)	1.4^{ii} (0.3%)
Vegetable fields	826±47$_d$	770±43 $_c$ (93.3%)	2.9±0.2 $_a$ (0.4%)	1.3±0.1$_a$ (0.2%)	49±3$_b$ (5.9%)	2.5±0.2$_a$ (0.3%)	0.9^{i} (0.1%)	1±0.4 (0.1%)	0.2±0.01 (0.02%)	1.2±0.05^{iii} (0.1%)

Denotations: NE-TP, total P in NaOH and EDTA extracts; NMR-P_i, inorganic P in NaOH and EDTA extracts; NMR-P_o, organic P in NaOH and EDTA extracts; Ortho-P, Orthophosphate; Pyro-P, Pyrophosphate; Poly-P, Polyphosphates; Monoester-P, Orthophosphate monoesters (Orthophosphate monoesters include Inositol–P); Inositol–P, Inositol phosphate; Myo-, Myo-inositol; Scyllo-, Scyllo-inositol; Diester-P , Orthophosphate diesters; PL, Phospholipid; Phos-P, Phosphonates; i, ii and iii represent the number of detected sample (1, 2 and 3); Parentheses indicate the average proportion to total P in NaOH and EDTA extracts; The values within a row for each property with the same letter are not significant at 5% level (Duncan)(Paper III).

3.1.7 Soil phosphatase activities

Phosphatases activities have been granted increased consideration within the fields of agriculture and environment in the recent year (Tabatabai and Fu 1992). This is mainly due to their catalysis of the hydrolysis of ester–phosphate bonds, leading to the release of bioavailable orthophosphate (Nannipieri et al. 2011). The activity of this enzyme needs therefore to be considered as an explanatory parameter when assessing the hydrolysis of soil organic P, and thereby its environmental impact (Newman et al. 2003). The phosphatases activities were found to be generally higher in forest and orchard soils than in cropland and vegetable fields (Fig.13). Tarafdar and Claassen (1988) reported soil phosphatases mainly originated from soil microbial organisms, while uncultivated or less uncultivated soils commonly have microbial activities due to less human disturbing. In the studied soils there were relatively low levels of acid phosphomonoesterases (AcP) and high levels of alkaline phosphomonoesterases (AlP). The governing factor here is most likely the circumneutral soil pH. Barbarić et al. (1984) reported that acid phosphatases have optimal activity at pH values from 3 to 4.5, while the average pH value of these soils were around 7, which is more suitable for the production of AlP.

Phosphodiesterases (PD) and pyrophosphatase (PY) activities were generally lower than AlP. The cause for this is most likely related to a limited availability of their respective substrates in the soils (Table 2).

There is no clear consistent trend in phosphatases activities between the four different land use types, though forest and orchard soils showed similar and relatively high phosphatases activities, whereas cropland and vegetable field soils had relatively low activities. The results indicate therefore that phosphatases activities were generally higher in uncultivated soils than in cultivated soils, which is consistent with previous studies (Acosta-Martinez et al. 2007, Zhang et al. 2012).

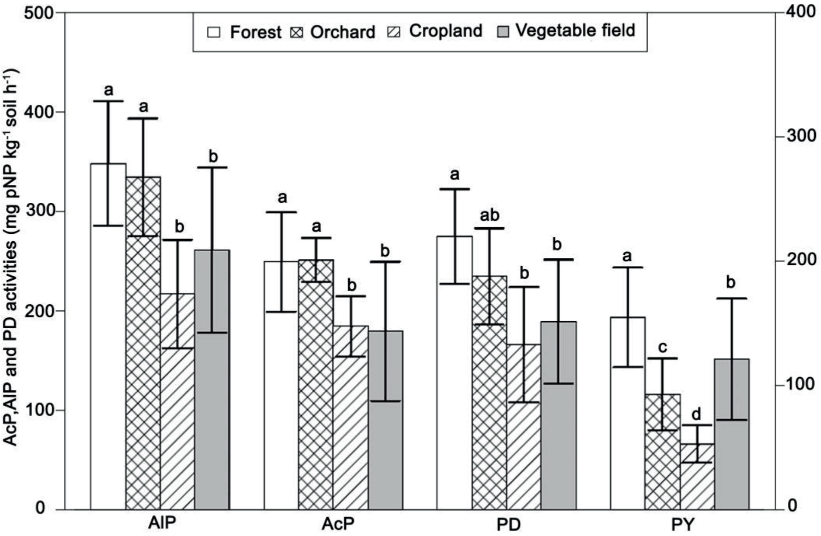

Figure.13 Soil phosphatases activities in soils from four land use categories. AlP, alkaline phosphomonoesterases; AcP, acid phosphomonoesterases; PD, Phosphodiesterases; Pyrophosphatase; same letter denote no significant difference at 5% significance level (Duncan) and error bars present the standard deviations (Paper III).

3.2 Modelling results

3.2.1 Spatial characteristics of the Amended P index model

The spatial distribution of amended P index values subdivided into five risk categories (very low, low, medium, high, and very high) is shown in Fig. 14. The index values and geographical factors were extracted from 6983 grid points (250 m × 250 m) in order to explore the spatial relationship between the values and corresponding factors. In Figure 15 the P index for each point is plotted against the distance to each individual village and watercourses, as well as its elevation. Most grid points are found in the regions with less than “medium” risk level categories. This implies that the critical source areas with a major potential for P loss are limited. All three geographic factors show a general decreasing trend with increasing P index level. Most of the grids with high and very high risk for P loss are therefore found in places that are located closer than 1 km from a village or less than 500 m from a river. A more significant negative trend was found for the elevation, indicating that most of the high and very high risk points are located at an elevation level less than 100 meters above the lake level. In general this translates to the plain lowland area, riverine zones and village regions, which thus represent the hot-spot source areas for P flux to the reservoir.

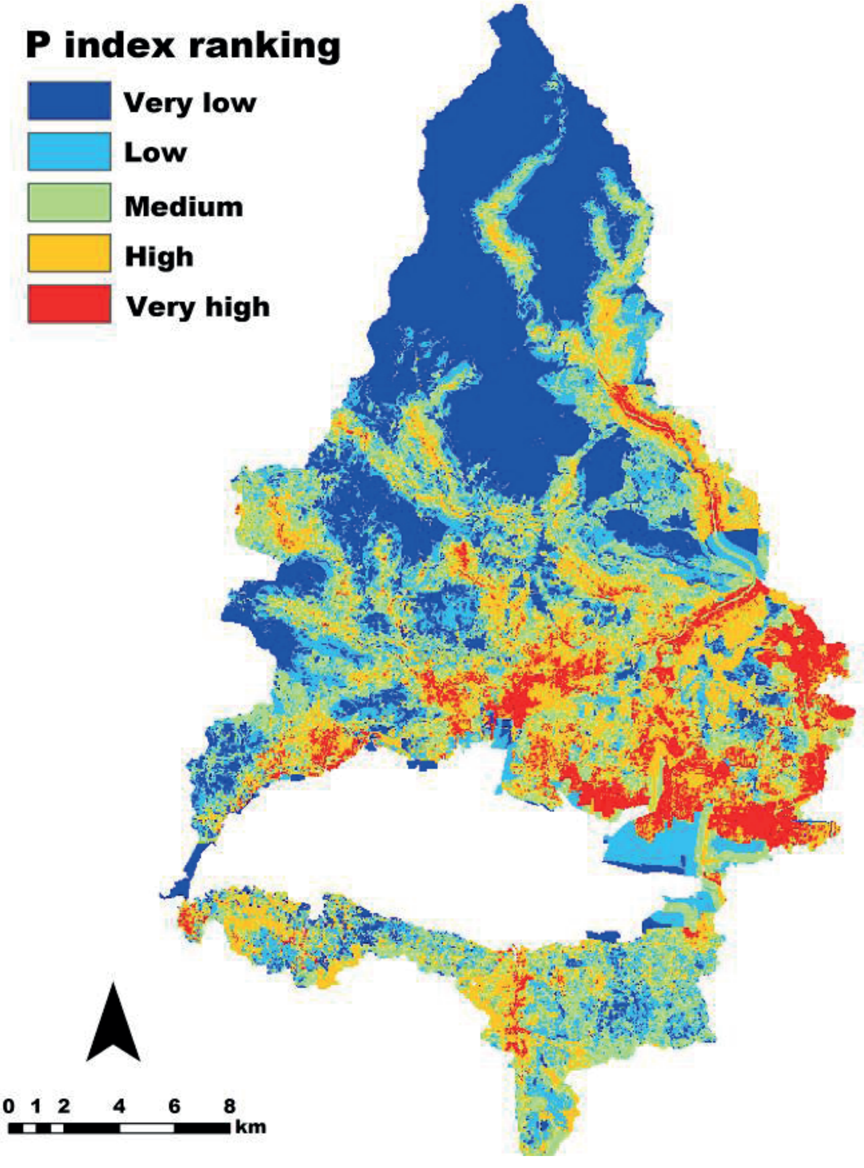

Figure.14 Spatial distribution of P index rating (Paper I).

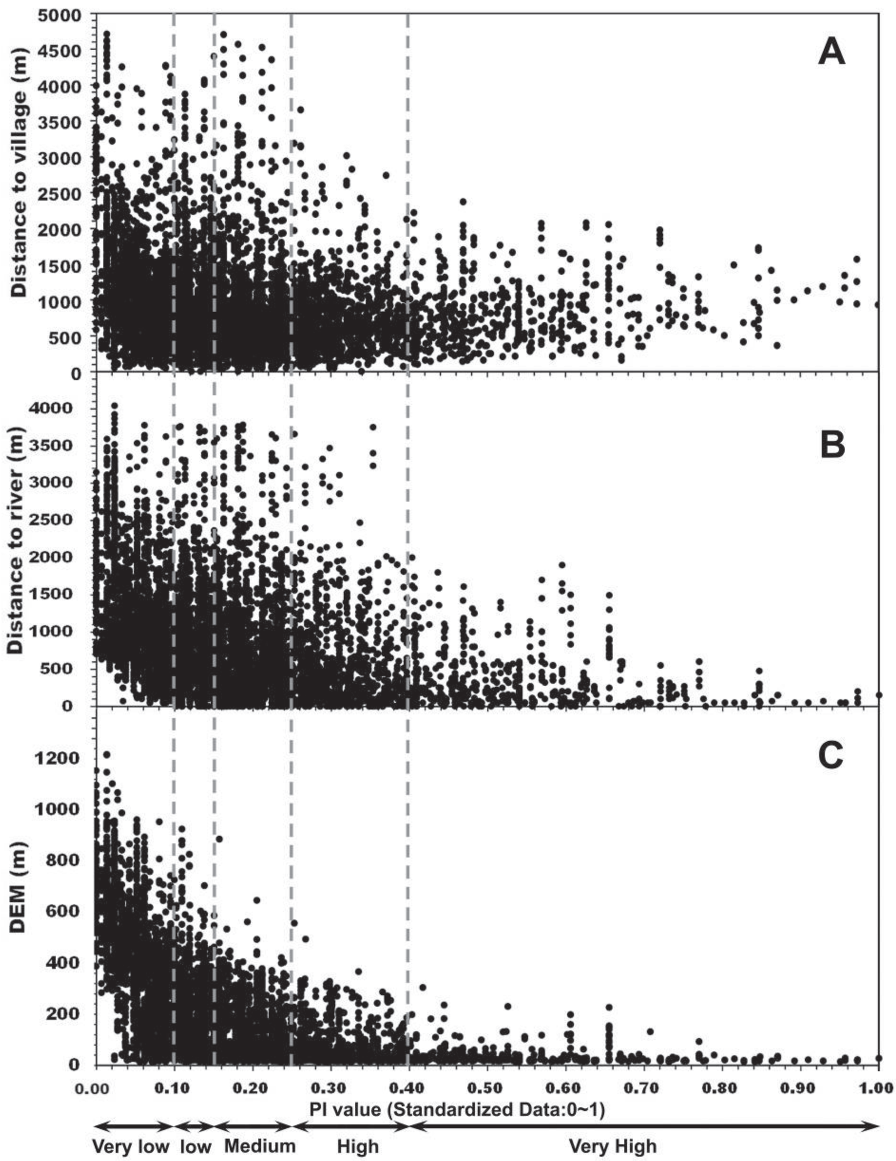

Figure.15 Spatial distributions of P index values relative to main explanatory geographic factors: (A) Distance to the each village; (B) Distance to each watercourse; (C) Elevation above reservoir level (Paper I).

3.2.2 Relative importance of input parameters to the P index model

The parameter sensitivity analysis revealed that the very high risk area is strongly governed by the source factors, i.e. high DPS and large fertilizer application revealed relatively high sensitivity scores (Fig. 16). Excess application of inorganic P fertilizers, and manure from the extensive livestock and poultry breeding, as well as sewage to the fields (JCBS 2012, JCEPB 2012) jointly contribute to a high level of P enrichment in the top soil. In addition, the degree of P saturation (DPS %) generally contributed significantly to a high risk level (average value ca. 21.5%) due to high concentration of bio-available P and the limited capacity of the soil to sorb P. Where there is a very high risk for P loss the runoff level and water course erosion factors are shown to have the greatest relative importance in the transportation scheme. The extent of low-lying terrain and density of agricultural draining networks has a strong influence on the potential risk for P loss. The riverine region should therefore be prioritized as the main target area for control strategies abating P loss.

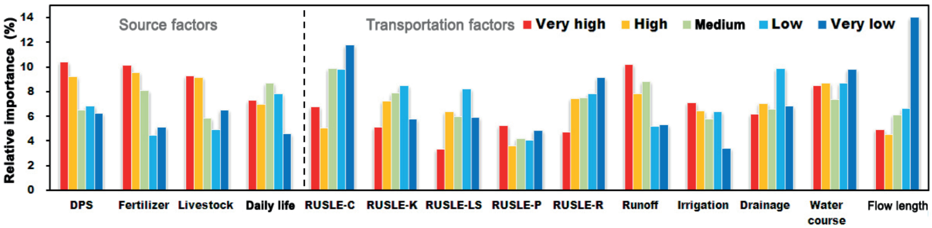

Figure. 16 Relative importance of the 14 input variables on the P index score based on Garson's algorithm (Paper II).

The high risk zone was also significantly influenced by agricultural activities, since agricultural land compromised 66% of the land use in the studied watershed. The P index score was therefore again mainly governed by the DPS, as well as the application of P fertilizer and livestock manure. The relative importance of DPS and application of P fertilizers factors are inherently correlated in the high and very high risk area. This is because the DPS is mainly governed by the application of fertilizer, since the soils phosphorus sorption capacity is relatively constant within the study area. Water course and runoff level factors had also relatively high sensitivities in the high risk areas. This emphasizes the significance of riverine agricultural areas in regards to controlling P transportation.

Medium risk areas are generally distributed in the intermediate region situated between the mainly natural and predominantly human-affected regions. Compared with the high risk areas, the proportion of farmland is significantly lower (19%) in the medium risk area, leading to lower sensitive scores for DPS and application of P fertilizer. Similarly, the relative importance of application of manure was significantly lower than in the high risk areas due to less livestock farming. On the other hand, the disposal of sewage showed the highest importance among the source factors. This is mainly because most residents live in this region. In regards to the transportation factors, vegetation coverage (RUSLE-C), slope-length (RUSLE-LS) and runoff level mainly govern the PI in the median risk zone. This reflects that the natural factors related to soil erosion have a greater influence on the potential for P loss than in the low-land area.

The influences of human activities in the low risk zone is less than in the medium risk zone due to a larger proportion of natural forest and shrub land (48%). This led to a low sensitivity of source factors on the PI, especially the application of P fertilizers and livestock manure. The analysis instead shows that the transportation factors govern the potential for P loss in this zone. Especially the draining class and soil texture (RULSE-K) factors, associated with soil physical properties, gained higher sensitivities. This is likely reflecting a greater diversity of soil types and slopes in this low risk area.

Similar to the low risk area, source factors have relatively weak sensitivity in the very low risk area. Due to its relatively rugged morphology the influences of human activities are low, with farmland and residential areas constituting only 2% and 5% of the very low risk area, respectively. Instead the transportation factors governed the potential risk for P loss: Flow length, vegetation coverage (RUSLE-C) and water course erosion showed high sensitive scores, with a record high score in relative importance for the flow length factor. This factor is the measure of the actual migration distance of surface runoff, which becomes larger as the terrain complexity increases as it does in this risk zone.

3.2.3 Modelling of land use change and corresponding water quality prediction

3.2.3.1 Accuracy assessment for spatial stimulation

The ROC values for the CLUE-S model ranged from 0.82 to 0.95. These close to unity values indicate that the spatial distributions of all land use types were satisfactorily explained by the selected driving variables.

Fig. 17 shows actual and simulated distribution of land use in 2006, 2009 and 2012, with Kappa values 0.88, 0.85 and 0.83, respectively. This high accuracy demonstrates that the Gray combination (GC) model coupled with CLUE-S model can be used to predict land use.

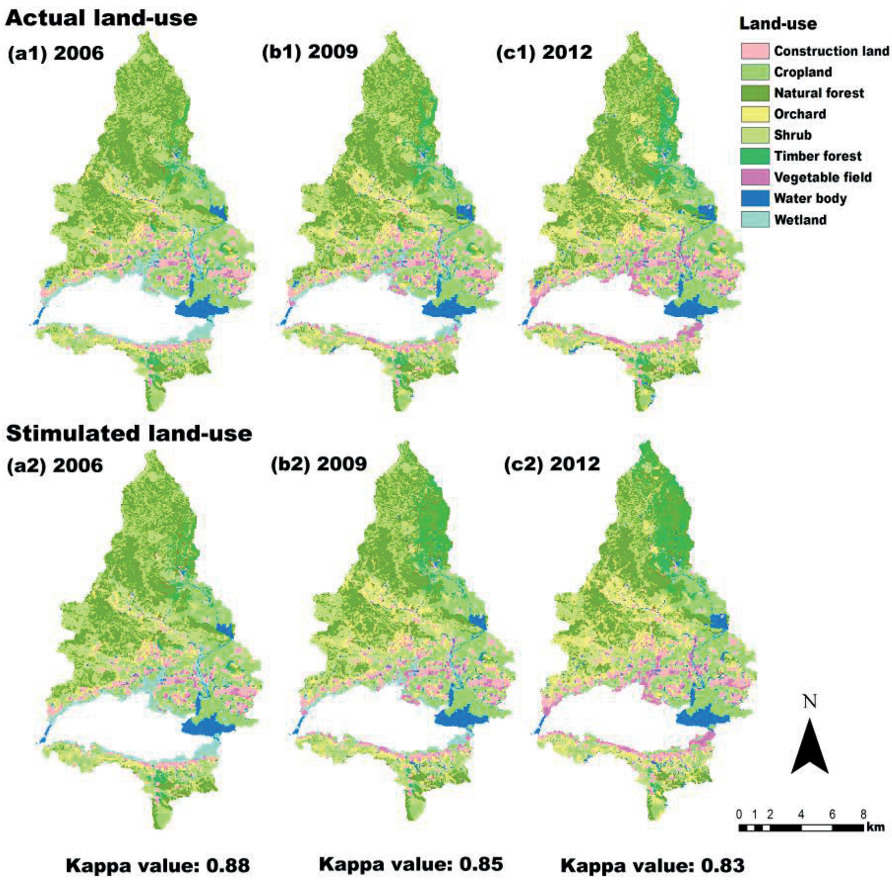

Figure. 17 Actual and simulated land use in year 2006, 2009 and 2012 (Paper IV).

3.2.3.2 Prediction of land use under different scenarios

Two scenarios were simulated in this study: Scenario 1 was 'business-as-usual' based on the existing land use development trend; In Scenario 2 the effects of the initiated local emigration and ecological restoration plan on the land use were assigned. The predicted area for each land use category in 2014, 2016 and 2018 under these two scenarios is shown in the Fig. 18 and spatial distributions of the land use are shown in

Fig.19.

In Scenario 1 a continued expansion of agricultural land use types and reduction of natural land use types is predicted. The increase in cropland and vegetable field mainly takes place close to the Yuqiao reservoir. Correspondingly, the existing natural wetland and shrub land will mainly be converted to farmland in this area. In mountainous areas the natural forest and shrub land will to a large extent be transformed into orchards and timberland.

In Scenario 2 the areas of natural land use (i.e. categories natural forest, shrub and wetland) are predicted to increase significantly (Fig.18). Moreover, the spatial structure of land use will change significantly. This is mainly due to that the extent of agricultural lands will be significantly decreased allowing the natural land use to become the dominating category.

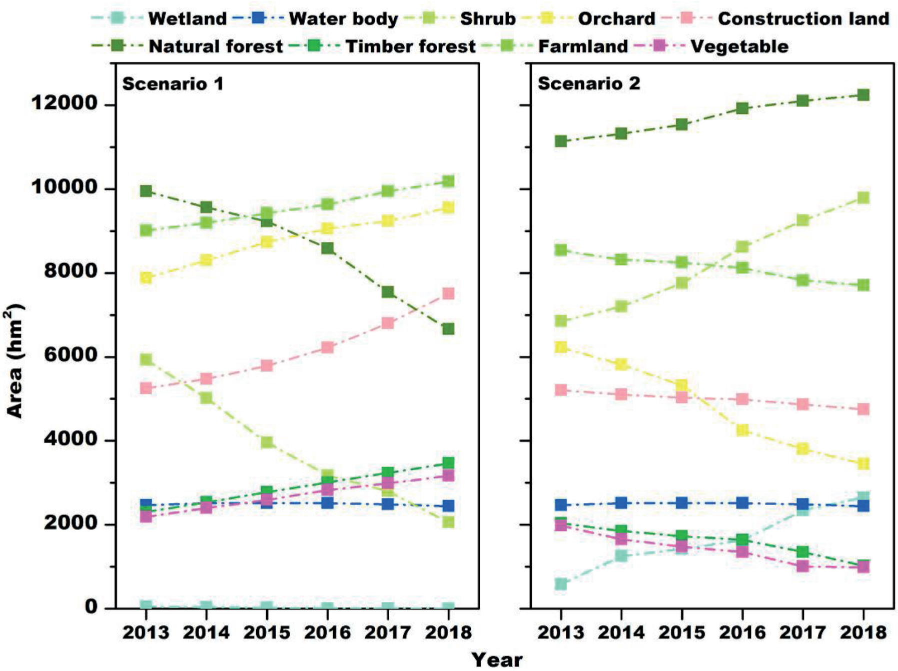

Figure.18 Predictions of area for each land use category (2013~2018) under 'Business-as-usual' (Scenario 1) and with the initiated abatement actions (Scenario 2)(Paper IV).

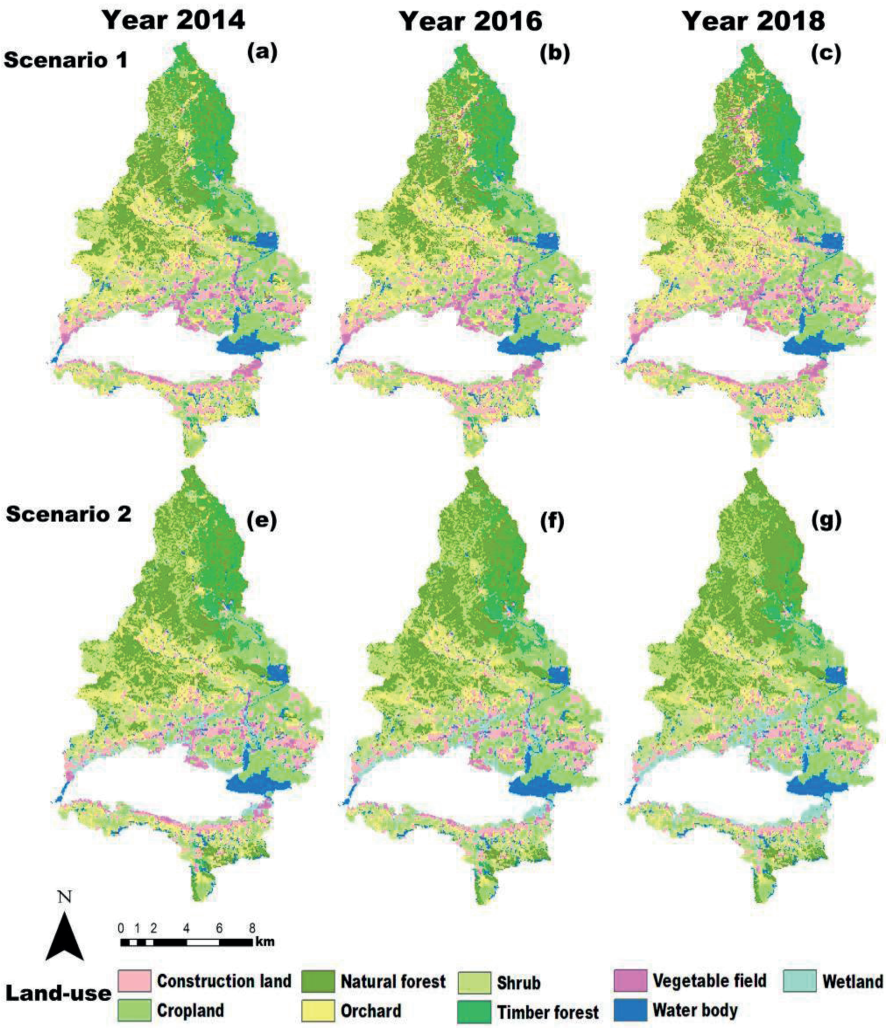

Figure.19 Simulated spatial distribution of land use in the local watershed of the Yuqiao reservoir for year 2014, 2016 and 2018 under 'Business-as-usual' (Scenario 1) and with the initiated abatement actions (Scenario 2) (Paper IV).

3.2.3.3 Prediction of water quality based on the developed land use index

(1) DPS weight coefficient for land use index

DPS was used as weight coefficient for the land use index due to its superior account of potential risk for loss of soil P than other P pools indicators (Sharpley 1995b, Schroeder et al. 2004). The data from the synoptic studies of soil physiochemical characteristics showed that the mean values for DPS are significantly different between the various land use types (Table 3). Mean value of DPS in forest fields is only slightly above 0.9%, while the corresponding value in vegetable fields is around 70.8%. Moreover, the coefficient of variation for DPS in each land use category is generally low (less than 22%), implying that the mean value has a relatively strong representation. The main cause for this is that the soil P content and its fraction characteristics are mainly governed by local agricultural practices over a long period.

Table 3
DPS% and Weight coefficient for land use changes in each of the land use types.

Land use	Number of soil samples	DPS%	Weight coefficient (Normalization)
Forest	10	$0.9 \pm 0.2_{a}$ (22%)	0.01
Shrub	11	$2.73 \pm 0.5_{ab}$ (18%)	0.05
Timber	8	$8.1 \pm 1.2_{bc}$ (15%)	0.1
Wetland	8	$14.7 \pm 2.2_{c}$ (15%)	0.2
Orchard	8	$33.2 \pm 4.5_{d}$ (14%)	0.5
Crop	13	$42.1 \pm 6.5_{e}$ (15%)	0.6
Vegetable	12	$70.8 \pm 15_{f}$ (21%)	1

DPS% values are given as mean ± standard deviation (coefficient of variation %). Values for DPS with different letters are significantly different at 5% level (Duncan).

(2) Water quality response based on the modified land use change index

In order to develop the water quality prediction model the land use index with DPS weight coefficients were related to P concentrations in the Yuqiao Reservoir. This assessment showed that both total P and orthophosphate concentrations are linearly correlated to the land use index with r^2 values above 0.85 and strong significance ($p<0.0001$) (Fig. 20). This strong explanatory capability is partly due to that the P concentrations in Yuqiao reservoir is mainly governed by P load from the local watershed (Zhang et al. 2003, TMWA 2010), and that the land use index with DPS weight coefficient is well suited as a proxy for the potential risk for soil P loss.

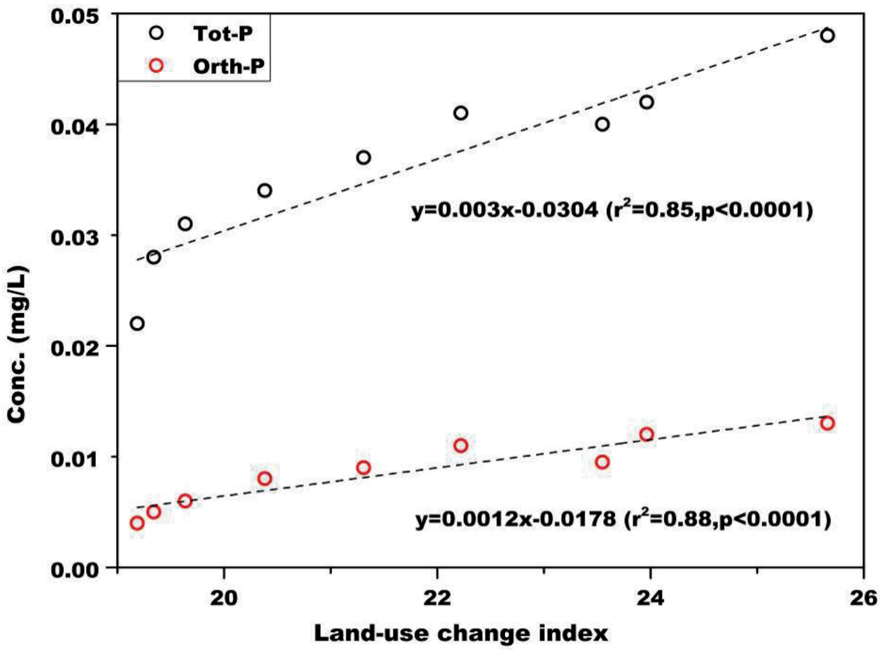

Figure. 20 Linear correlation between the land use index and the P concentration in the reservoir (Paper IV).

(3) Prediction of water quality change

Total P and orthophosphate concentrations in Yuqiao reservoir were simulated (year 2013~2018) under the two land use change scenarios based on the model predictions of land use change in Chapter 3.2.3.2 (2).

For the 'business-as-usual' scenario (Scenario 1) the concentrations of total P and orthophosphate is predicted to increase to 0.074 and 0.024 mg L^{-1}, respectively, by 2018. It is thus apparent that eutrophication in the reservoir will increase strongly if no abatement actions are taken.

The initiated abatement actions, including emigration and ecological restoration, will according to the model significantly reduce the P concentrations in Yuqiao reservoir. The model predicts that by implementing the plans the total P and orthophosphate concentrations will within 2018 be reduced by 36% and 45%, respectively, relative to the year 2012. Total P and orthophosphate concentrations will then be 0.032 and 0.007 mg L^{-1}, respectively. This concentration of total P is just slightly below the value defined by OECD as a eutrophic water body (0.035 mg L^{-1}) (Vollenweider 1982).

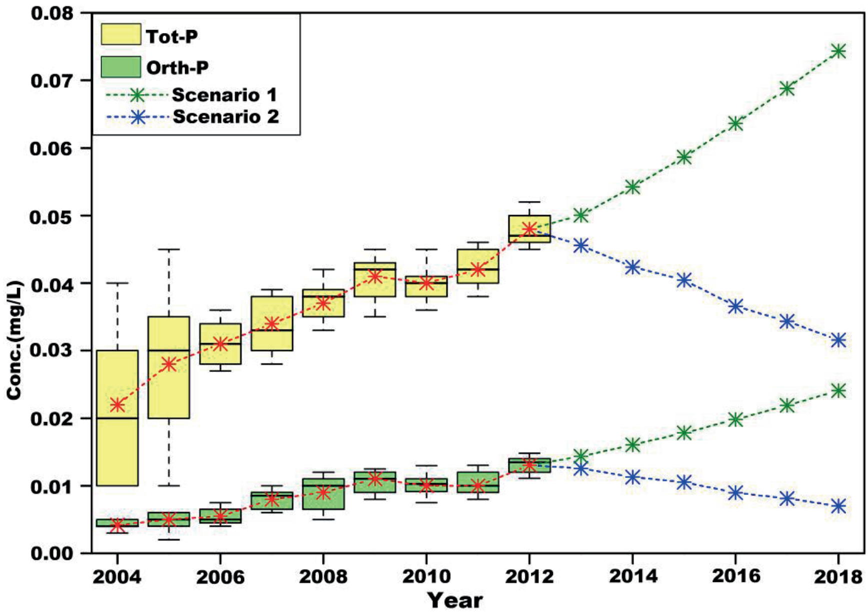

Figure. 21 Prediction of concentrations of total P and orthophosphate P in the Yuqiao reservoir assuming 'Business-as-usual' (Scenario 1) and with initiated abatement actions (Scenario 2)(Paper IV).

4. Conclusions

The main findings in this thesis are:

(1) Identification of potential risk for P loss using an amended P index model

It was possible to improve the assessment of the potential loss of P by amending the P index scheme. The precision of the P index scheme was greatly enhanced by refining the spatial resolution of input data to the scale of village unit, introducing more specific indicators in both source and transport system, and re-adjusting the organization structure of the index. The amended P index scheme is demonstrated to have the capability of capturing the spatial differences in loss of P fractions from watersheds with different land use.

In regards to the study site, believed to be generic for an agricultural dominated region in northern China, the areas in the vicinity of the reservoir and rivers, the plain lowland area and land surrounding the villages generally constitute a relatively high potential risk for P loss. In regards to different land use the study demonstrates that farmlands have the highest potential risk for loss of P. The areas with “very high” and “high” potential for P loss account for only a small proportion (29%) of total study area. This emphasizes the need to have specifically targeted and differentiated abatement actions, rather than inducing a general “flat” target goal.

(2) Determining the relative significance of the explanatory factors on the final P index value within different risk zones

Source factors generally show high sensitivities in the zones with very high and high risk for P loss. The degree of P saturation appeared to be governed by the amount of applied P as fertilizer. As the main mechanisms for P transportation is by hydrological processes, the runoff level and water course erosion factors also exhibit relatively significant sensitivities in the transportation scheme. This clearly reflects the importance of considering the combined effects of explanatory variables in the revised P index;

In the transition zone, between predominantly natural and human-affected regions, the average sensitive score of source factors and transportation factors were similar. P emission from sewage and fertilization of orchards were the main sources and thus main factors governing the P index value. The most important factors influencing on the transportation were vegetation coverage and runoff level;

In the low and very low risk zones the potential risk for P loss was mainly governed by factors influencing on the transportation, especially the vegetation coverage (RUSLE-C) and flow length. This is mainly due to strong erosion factors and overall low source factors.

(3) Using land use as explanatory factor for the potential risk of P loss by assessing differences in P indices and their governing parameters

Soil P pools and P species are significantly affected by long-term application of excess mineral- and organic fertilizers. TP, TIP and STP showed a consistent increasing trend between different land use categories according to the following order: forest < orchard < cropland < vegetable field soils. This land use sequence is consistent with the degree of agricultural management intensity including application of P fertilizers.

Relatively coarse soil texture, predominance of 1:1 type clays and poor organic matter content render the soils with poor P sorption capacity. This together with a heavy loading of P caused STP to hold strong explanatory power as a DPS indicator. Considering the measured DPS values relative to its critical threshold value (25%) reveals a large potential risk for soil P loss from the studied cropland and vegetable field soils. Moreover, such intensively cultivated lands are normally situated in close proximity to the surface water reservoirs.

Soil phosphatase activities were higher in forest and orchard soils than in cropland and vegetable field. AlP constituted the strongest phosphatases activity due to a circumneutral soil pH. This implies that it may constitute a potential environmental risk through the hydrolysis of monoester-P. Orchards soils possess both high monoester-P content and AlP. Based on this it is recommended to the authorities to pay more attentions to the orchard field in our study area.

These results demonstrate that the type of land use can be generally used as the explanatory factor for assessing potential risks of phosphorus loss from soils.

(4) Using land use change to predict the P level of receiving water bodies

Simulation of land use changes showed that the developed Grey combination (GC) model predicts more accurately the land use change than the original GM (1.1) model. This is mainly due to that the GC model also considers the influence of driving factors. Moreover, a good prediction was also achieved for the spatial distribution of the land use, with final Kappa coefficient greater than 0.83 for the validation period. Two scenarios of land use change were predicted: ‘Business as usual’ and with the implementation of the introduced emigration and ecological restoration plan.

The land use index with DPS weight coefficient was found to be strongly correlated to the P concentrations in runoff water. Applying this strong correlation to the modelled changes in land use allowed a prediction of changes in P concentration in the reservoir. The scenario with introduced abatement actions indicates that the concentration of total P and orthophosphate will be reduced by 36% and 45% by 2018, relative to 2012. This model provides a simple, yet effective, management tool for policy makers, which can aid environmental managers to identify risk for eutrophication as well as assist policy makers to assess the ecological and environmental effect of changes in land use.

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